THE MECHANISM OF ION EXCHANGE ON A SYNTHETIC RESIN, AND THE APPLICATION OF CATION ACTIVITY COEFFICIENT RATIOS TO THE INTERPRETATION OF ION EXCHANGE EQUILIBRIA

by

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PART I

AN INVESTIGATION OF THE MECHANISM OF CATION EXCHANGE

Introduction

Early research in the field of cation exchange was concerned with the investigation of naturally occurring exchangers such as zeolites, or exchangers such as alkali-leached greensand or sulfonated coal which were formed from naturally occuring products. These exchangers, however, were unsatisfactory because of their low exchange capacity and their instability in certain solutions. Recent research has been concerned with synthetic cation exchangers, including resins of the polyhydric phenol-formaldehyde condensation type and sulfonated hydrocarbon resins of the polyvinyl or polystyrene type. These types are represented, respectively, by the Amberlite-IR resins and by Dowex-50. Since these resins possess more of the properties necessary for a quantitative study, their investigation yields data of greater interest and significance than those obtained in the earlier work.

Boyd and co-workers (1), in their investigations of a phenol-formaldehyde resinous exchanger, show that heterogeneous cation exchange processes may be formulated either in terms of the Langmuir adsorption mechanism or according to the law of chemical equilibrium, and that the two methods

of formulation are formally equivalent. Bauman (2) has shown that equilibrium data may also be interpreted in terms of the Donnan concept of membrane diffusion. For dilute solutions, however, quantitative agreement with the theory is not obtained. The most satisfactory and convenient treatment, however, is that based upon the law of chemical equilibrium (1, 2, 3, 4, 5).

Thus, in the simplest case, when both of the cations are univalent, let us consider the reaction to be that represented by the equation

$$A^+ + BR \rightleftharpoons B^+ + AR$$

where A^+ and B^+ are the cations involved in the exchange, and R represents the active anionic portion of the insoluble resin.

From a purely thermodynamic viewpoint, then, and regardless of the structure of the resin, the following equation should be applicable:

$$\frac{a_{B^+}\ a_{AR}}{a_{A^+}\ a_{BR}} = K$$

where a_{A^+} and a_{B^+} are the activities of the respective ions in the solution, a_{AR} and a_{BR} are the activities of the two resin components when equilibrium has been attained, and K is the equilibrium constant. As a matter of convenience, when the activity coefficient data are not available, a "concentration equilibrium quotient," K_c, may be defined by

the equation

$$K_c = \frac{C_{B^+} \; N_{AR}}{C_{A^+} \; N_{BR}}$$

where C represents the concentration of an ion in the aqueous solution and N represents the mole fraction of the resin component in question in the resin phase. Equilibrium data which were obtained in this portion of the ion exchange investigation will be tabulated in this form.

It has been assumed by most of the workers in this field that the over-all process occurring when a sample of an ion-exchange resin is immersed in a solution of electrolytes can be formulated in terms of such a simple equivalent exchange; that is, one equivalent of B^+ has usually been supposed to enter the solution from the resin for every equivalent of A^+ that enters the resin from the solution, the volume of the solution meanwhile remaining constant, so that the concentrations of both ions in the equilibrium solution, as well as the equilibrium composition of the resin, can be determined from a knowledge of the original concentrations and analysis of the final solution for one of the cations only. In some of the most recent studies (2, 4, 5) the possibility of non-equivalence of exchange has indeed been mentioned, but it has been given little consideration. Duncan and Lister mention the possible adsorption of non-exchanged material on the surface of the resin, but their calculations

are based on the experimental determination of the mole fraction of only one cation in each of the phases at equilibrium and consequently on the assumption of equivalence of exchange. Marinsky asserts that he has established the occurrence of equivalent exchange under the conditions of his experiments. However, on close examination of his data it appears that by using small quantities of resin he has merely reduced the discrepancy in the number of equivalents of electrolyte in the solution before and after exchange; and by increasing the volume of the solution he has limited the experimental error in the determination of the total number of equivalents of electrolyte to an order of magnitude no greater than this discrepancy. Bauman and Eichorn observed that when the water-wet hydrogen form of Dowex-50 is immersed in hydrochloric acid, the chloride concentration in the external solution, when equilibrium has been reached, is always found to be greater than in the solution within the resin particles, often in a ratio as high as 10: 1. When dry acid resin was introduced into 1 molar hydrochloric acid, they observed a considerable increase in the chloride ion concentration of the external solution. Their calculation of the equilibrium constant for any particular exchange is, however, again based on the analysis for one ion only in the solution phase, and the assumption of equivalence of exchange.

On the other hand, Lowen and Stoenner (6), in their

recently completed work, report that equivalence of exchange, as ordinarily understood, is apparently never obtained. They determined experimentally, for each exchange, the concentrations of the two exchanging cations in both the initial and the equilibrium solutions. In almost every instance, the concentration of the solution was found to undergo an appreciable net increase during the exchange. They attributed this increase to the preferential absorption of water from the solution by the partially dried resin. From relations based upon the conservation of the resin anion and the two cations, the apparent decrease in the volume of the solution due to water absorption was calculated, and this change in volume was taken into consideration in the calculation of the composition of the resin phase at equilibrium. In all the exchanges involving either silver or thallous ion, however, they found that the apparent inequality of exchange could not be accounted for solely in terms of this postulation of water absorption. The apparent discrepancy was, in general, smaller, and decreased, in fact changing sign, as the concentration of silver or thallous ion in the equilibrium solution increased. This behavior they attributed to adsorption of the cation by the resin, in addition to simple exchange and water absorption. In order to calculate the equilibrium resin composition and the cation adsorption effect, they assumed exact equivalence in the actual exchange

process, and constant water absorption for any resin throughout a series of experiments.

It was the purpose of this investigation to attempt to determine with greater certainty the cause of the change of the ionic strength of the solution, as reported by Lowen and Stoenner (6), accompanying the exchange of ions.

Experimental Methods

Preparation of Resins---For the study of each exchange reaction, two "pure" resins were prepared, one containing each of the cations involved in the exchange. In some cases these resins were dried in a vacuum desiccator over phosphorus pentoxide at room temperature; other samples were merely air-dried. No attempt was made to attain any specified moisture content, but in each case the approximate degree of dryness was regulated according to the experiment for which the resin was to be used. The number of grams of partially dried resin containing one gram-equivalent of exchangeable cation was designated as the equivalent weight of the resin. The equivalent weight of each resin, as thus defined, was determined by an appropriate method to be described below.

Hydrogen Resin---The pure hydrogen form of Dowex-50 was prepared by percolation of hydrochloric acid of constant boiling point, under a reflux condenser, through the commercial product in a column 5 cm. in diameter and 70 cm. in height. This treatment was continued until the effluent solution gave no further flame test for sodium ion. The product was then washed with distilled water until the washings showed only a negligible content of chloride ion, and dried to an arbitrary extent. The equivalent weight of the dried resin was determined in the following manner. A weighed quantity was placed in about 25 ml. of saturated sodium chloride so-

lution. When equilibrium had been reached, the liberated hydrogen ion in the salt solution was titrated with standard sodium hydroxide solution, methyl red serving as the indicator. The mixture was then again allowed to stand until a new equilibrium had been attained, whereupon the titration was repeated. This process of alternate equilibration and titration was continued until a non-fading endpoint was reached.

Ammonium Resin---Pure ammonium resin was prepared from the hydrogen form by treatment with a large excess of saturated ammonium chloride solution, the liberated hydrogen ion being neutralized with ammonium hydroxide solution. The exchange was regarded as complete when the pH of the solution remained constant and equal to that of saturated ammonium chloride solution. The equivalent weight of the ammonium resin was determined by treatment of a weighed quantity with saturated sodium chloride solution. Pellets of sodium hydroxide were added to the resulting solution, and the ammonia formed was distilled into a measured volume of standard acid. After all of the liberated ammonia had been collected, the excess acid was titrated with sodium hydroxide solution.

Silver Resin---For the preparation of pure silver resin, hydrogen resin was placed in the column previously described, and 1 molar silver nitrate solution was passed through it. The liberated hydrogen ion in the effluent solution was

neutralized by vigorous agitation with an excess of freshly prepared silver oxide. After neutralization, the solution was filtered and again used as influent. Conversion to silver resin was regarded as complete when the pH of the effluent solution showed no more than a negligible decrease from that of the influent. The equivalent weight of the silver resin was determined by treatment of a weighed quantity, in a small column, with 200 ml. of saturated sodium nitrate solution, which was allowed to percolate through the resin at the rate of about one drop per second. An aliquot portion of the effluent solution was then titrated with standard potassium iodide as the precipitating agent (7).

General Method---In the exchange experiments, weighed samples of the resins to be studied were placed in ground-glass stoppered flasks in contact with portions of a series of accurately analyzed aqueous solutions of the appropriate salts of the cations involved, in varying proportions but at a constant total ionic strength of 1 molar. As it was necessary to know precisely the volume of solution which was added in each case, a calibrated pipette was used. The attainment of equilibrium was hastened by agitation on a mechanical shaker, which was immersed in a constant temperature bath maintained at $25.0 \pm 0.2^{\circ}$; equilibrium was reached, in every case, within two hours.

Equilibrium Solution---The concentration of each cation in the aqueous solution at equilibrium was determined by

means of a direct analysis such as those described above.

Equilibrium Resin---The washed equilibrium resin was analyzed for each cation by means of complete exchange of both for sodium ion, by treatment with sodium chloride or sodium nitrate and sodium hydroxide solutions. The experimental procedure was essentially the same as that described for the determination of the equivalent weight of the resin.

Adsorbed Electrolyte---When it was desired to determine the quantities of electrolytes which had been adsorbed on the resin, the procedure just described was modified in the following manner. After equilibrium had been attained, the aqueous solution was decanted off the resin. The equilibrium resin was filtered, with suction, and dried by pressure between layers of filter paper. The dried resin was then thoroughly washed with distilled water, and the washings were analyzed for both cations, in order that the quantities which had been adsorbed might be determined. In all cases the resin was washed a second time as a precautionary measure, but one washing was found to be sufficient in every instance.

Ammonium-Hydrogen Exchange

When the investigation of this exchange was begun, two samples of crude Dowex-50 were available. The first, which will be called resin A, was used in the earlier research in this laboratory and in most of the ammonium-hydrogen exchange work to be described. The second, which will be called resin B, was received from the Dow Chemical Company approximately 18 months later. It was used in a few of the later ammonium-hydrogen exchange experiments, and in all subsequent exchange work. Pure hydrogen and ammonium resins were prepared as described previously.

In the preliminary work on ammonium-hydrogen exchange, a weighed sample of pure hydrogen or ammonium resin, dried over phosphorus pentoxide, was allowed to come to equilibrium, in the manner already described, with a measured volume of solution containing known concentrations of hydrochloric acid and ammonium chloride. Analyses were carried out for both cations in the equilibrium solution and in the washed equilibrium resin. The purpose of these experiments was to test the assumption of equivalence of exchange (or of constancy of the capacity of the resin), and to determine whether or not the equilibrium composition of the resin could be calculated by attributing the change in ionic strength of the solution to absorption of water alone. The results of

a typical calculation based on these experiments are given below.

Initial Resin (NH_4 Resin): ..... 0.00398 gram-equivalent

Initial Solution: Volume ..... 24.97 ml.

HCl conc. ..... 0.9409 N

Amount of HCl ... 0.02349 gram-equivalent

Equilibrium Solution: HCl ..... 0.8256 N

NH_4Cl ..... 0.1270 N

Total ..... 0.9526 N

If it is assumed that the increase in ionic strength of the solution is due solely to absorption of water by the resin, it follows that the total number of equivalents of HCl and NH_4Cl in the equilibrium solution must be the same as the number of equivalents of HCl in the initial solution. From the analysis of the equilibrium solution, the ratio of HCl to NH_4Cl must be 0.8256: 0.1270.

Equilibrium Solution: HCl ..... 0.02036 eq. (calcd.)

NH_4Cl .... 0.00313 eq. (calcd.)

Ions Exchanged: .... 0.00313 eq.

Equilibrium Resin:	Calculated	Observed
H Resin ..	0.00313 eq.	0.00302 eq.
NH_4 Resin..	0.00085 eq.	0.00095 eq.
Total	0.00398 eq.	0.00397 eq.

The above experiments led to the following conclusions. (1) There was no change in the capacity of the resin during

exchange. That is, the number of equivalents of hydrogen resin plus the number of equivalents of ammonium resin after the exchange was the same as the number of equivalents of pure ammonium resin before the exchange. (2) On the assumption of equivalence of exchange, the validity of which was thus indicated, it was not possible to determine correctly the composition of the equilibrium resin solely by attributing the observed change in ionic strength of the solution to the absorption of water by the resin. Analyses of the solution for chloride ion both before and after the exchanges established that the increase in total cation concentration was paralleled by an increase in chloride ion concentration. This indicated that the increase in ionic strength was not due to any decomposition of the resin. In order to eliminate the possibility that the increase in chloride ion concentration might have been due to the presence of adsorbed chloride ion on the supposedly pure resins, samples of pure hydrogen and ammonium resins were decomposed by the sodium fusion method. Analysis of the decomposition products showed the absence of any chloride ion.

In order to account for the discrepancy between the composition of the resin as calculated on the sole assumption of water absorption, and the observed composition of the equilibrium resin, as well as for the change in total ionic strength of the solution, it was postulated that both adsorption of electrolyte and absorption of solvent by the

resin might take place. Accordingly a further group of experiments was conducted in which an additional analysis such as has been described under "Experimental Methods" was made for the quantities of both electrolytes which had been adsorbed by the resin. These experiments supplied the information which seemed necessary for the calculation of the amount of water absorbed by the resin phase.

A typical calculation is as follows:

Initial resin (H Resin) ..... 0.00504 gram-equivalent

Equilibrium resin (analysis)

H Resin....0.00077 eq.
NH_4 Resin..0.00428 eq.
Total.....0.00505 eq.

Electrolyte adsorbed by resin (analysis)

HCl.....0.000041 eq.
NH_4Cl.....0.000117 eq.
Total.....0.000158 eq.

Initial Solution:

Volume.....24.97 ml.
NH_4Cl conc..... 0.9845 N
Amount of NH_4Cl.0.02458 eq.

Equilibrium Solution:

Analysis:

HCl conc.....0.1747 N
NH_4Cl conc.....0.8321 N
Total.....1.0068 N

Amount of HCl...0.00504-0.00077-0.00004 = 0.00423 eq.

Amount of NH_4Cl.0.02458-0.00012-0.00428 = 0.02018 eq.

Total..... 0.02441 eq.

Volume (calcd)

From conservation of H^+... $\frac{0.00423}{0.1747}$ X 1000 = 24.21 ml.

From conservation of NH_4^+.. $\frac{0.02018}{0.8321}$ X 1000 = 24.26 ml.

Mean.....24.24 $\pm$ 0.025 ml.

Water absorbed by resin... 24.97-24.24 = 0.73 $\pm$ 0.025ml.

Water absorbed/eq. resin.. $\frac{0.73}{0.00504}$ = 144 $\pm$ 4 ml.

Initial water in resin (42 ml./eq.) = 0.21 ml. (From weight loss on drying at110° C.)

Final water in resin.....0.94 $\pm$ 0.025 ml.

Total water in resin/eq. resin... $\frac{0.94}{0.00504}$ = 186 $\pm$ 5 ml.

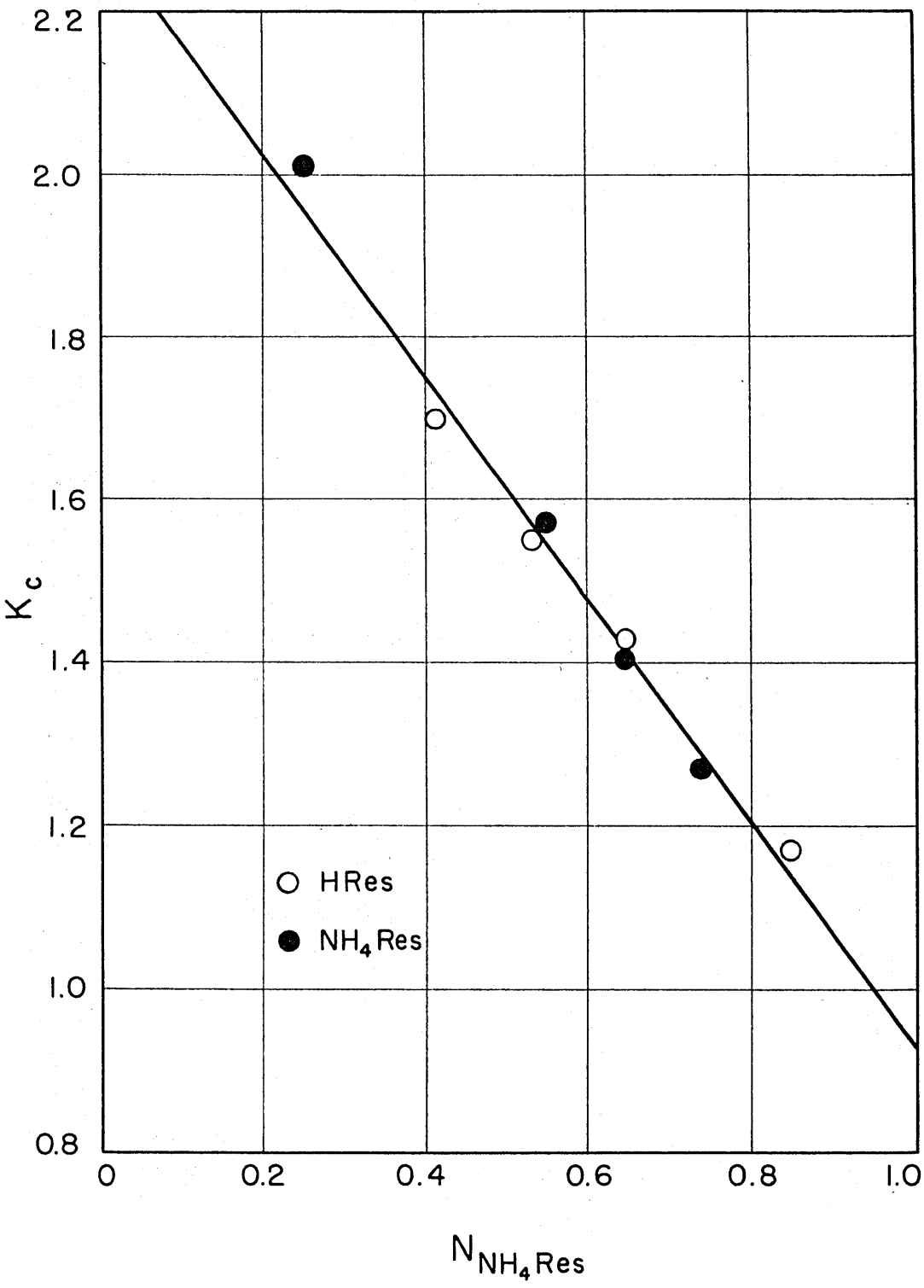
The results which were obtained from this type of calculation are presented in Table 1, and a plot of the variation of K_c with resin composition is shown in Figure 1. It can be seen that the values of K_c vary regularly from approximately 2.3 to 0.9 over the entire range of resin compositions. Thus they agree fairly well with the values of 2.6 to 1.0 over the same range of compositions which were calculated by Lowen and Stoenner (6). The data in Table 1 show no definite relationship between the resin composition and the total quantity of electrolyte adsorbed by the resin. The latter is probably a complex function of the relative tendency of the hydrogen and ammonium ions to be adsorbed, as well as of the capacity for adsorption of a resin of any given composition. For each electrolyte, however, the amount of

Table 1

Data On Ammonium-Hydrogen Exchange
(Resin A)

			(a) H Resin		
Mole fraction NH_4 resin at equilibrium	0.000	0.413	0.520	0.649	0.850
Equivalents HCl adsorbed per equivalent of resin	0.020	0.028	0.028	0.014	0.008
Equivalents NH_4Cl adsorbed per equivalent of resin	-----	0.009	0.016	0.015	0.023
Total equivalents electrolyte adsorbed per equivalent of resin	0.020	0.037	0.044	0.029	0.031
Initial water in resin (ml.) per equivalent of resin	42	42	42	42	42
Water absorbed (ml.) per equivalent of resin	144	135	167	125	144
Total water in resin (ml.) per equivalent of resin	186	177	209	167	186
$K_c = \frac{(H^+)(NH_4 Res.)}{(NH_4^+)(H Res.)}$	---	1.70	1.55	1.43	1.17
			(b) NH_4 Resin		
Mole fraction NH_4 resin at equilibrium	0.262	0.551	0.647	0.746	1.000
Equivalents HCl adsorbed per equivalent of resin	0.020	0.018	0.019	0.013	-----
Equivalents NH_4Cl adsorbed per equivalent of resin	0.005	0.011	0.017	0.021	0.032
Total equivalents electrolyte adsorbed per equivalent of resin	0.025	0.029	0.034	0.034	0.032
Initial water in resin (ml.) per equivalent of resin	55	55	55	55	55
Water absorbed (ml.) per equivalent of resin	90	97	91	101	87
Total water in resin (ml.) per equivalent of resin	145	152	146	156	142
$K_c = \frac{(H^+)(NH_4 Res.)}{(NH_4^+)(H Res.)}$	2.01	1.57	1.41	1.27	---

Fig. 1



adsorption is roughly proportional to the concentration of that electrolyte in the solution. Further, there is seen to be a considerable variation in the volume of water absorbed by each resin in the several exchange reactions, and also in the total volume of water held by the resin at equilibrium. In all cases, however, the greater absorption is shown by the hydrogen resin. It was thought that amount of absorption might possibly be influenced by the particle size of the resin and by its water content before exchange. It was noted that the resin particles crack upon wetting if the resin has previously been thoroughly dried. Of the two resins used for these exchanges, the ammonium resin was the less thoroughly dried and consisted of the larger particles.

In order that the effect of particle size upon the exchange reaction might be investigated, a batch of hydrogen resin was prepared from the crude Dowex-50 which had been most recently received (Resin B). It was then separated according to particle size by means of sieves and each fraction was treated in the manner described under "Experimental Methods". In order that the composition of the resin might not be changed, pure hydrochloric acid was used as the initial solution. The absorption of water by each sample was calculated by the method previously described, from the increase in ionic strength of the equilibrium solution. The results of this experiment are re-

ported in Table 2. As these results show solvent absorption to be practically independent of particle size, all subsequent work was done on resin of 14-28 mesh.

Two samples of hydrogen resin were then prepared from the same sample of crude Dowex-50. These samples were similar as to particle size, but were dried for different lengths of time in order that they might contain different amounts of water. After analysis to determine water content, a weighed sample of each was placed in hydrochloric acid solutions and the absorption was calculated as above. Results of total calculated water absorption on these resins are given in Table 3.

In order that the calculated absorption of water by the resin might be verified by a more direct method, the following experiment was conducted. After the resin had been placed in water and allowed to become saturated, it was dried by pressure between layers of dry filter paper. The loss in weight upon drying at 115° was then determined. This analytical procedure was used on hydrogen and ammonium resins prepared from both samples of crude Dowex-50 available in this laboratory, as well as on samples of resins of intermediate composition prepared from newer Dowex-50. These mixed resins were prepared by treating pure hydrogen or ammonium resins with hydrochloric acid or ammonium chloride solution as required. Intermediate resins of the same composition were shown to possess the same ab-

sorption capacity, regardless of whether they were initially formed from hydrogen or ammonium resin. As is evident from Table 4 and Figure 2, there is for each initial resin sample a linear relationship between the resin composition and the amount of water absorbed upon immersion.

At this point it was noted that there was satisfactory agreement between the solvent absorption capacity of the resin as determined on the one hand by this direct method, and on the other as calculated from the increase in ionic strength of the solution, only when no exchange occurred; that is, when hydrogen resin was placed in hydrochloric acid solution or when ammonium resin was placed in ammonium chloride solution. When exchange occurred on hydrogen resin, the solvent absorption as calculated from increase in ionic strength was too high; with ammonium resin, it was too low. This observation indicated that the discrepancy might be due to a change in volume of the solution when electrolytes of different apparent molal volume were exchanged. In an effort to verify this hypothesis, the change in volume upon complete exchange of ions was calculated for one liter of solution containing originally one gram-equivalent of hydrochloric acid or of ammonium chloride. Densities were taken from the International Critical Tables.

As an example, consider as the initial solution one liter of 1 N ammonium chloride. Since its density is 1.0146, the solution weighs 1014.60 g.

Table 2

Effect of Particle Size of Resin on Water Absorption

Particle size of resin (mesh)	14-20	20-28	35
No. of equivalents of resin used	0.00558	0.00591	0.00399
Water absorbed (calc., ml./eq.)	149	151	147

Table 3

Effect of Initial Water Content of Resin on Water Absorption

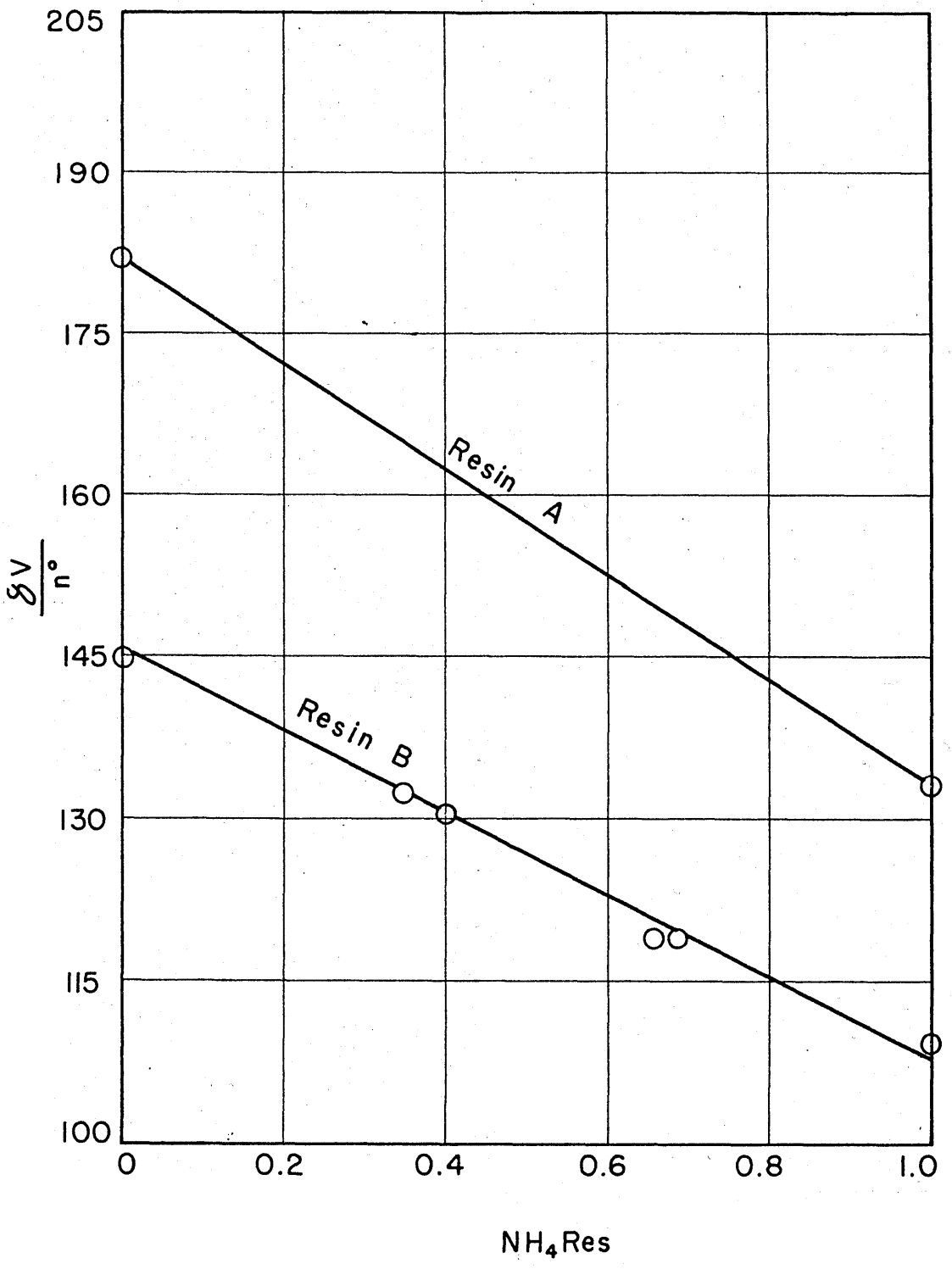
	No. of equivalents of resin used	Initial water content (ml./eq.)	Water absorbed (ml./eq.)	Final water content (ml./eq.)
H resin No. 1	0.00856	36	112	148
H resin No. 2	0.00557	117	32	149

Table 4

Water Absorption Capacity of Resin

Resin	Mole fraction NH_4 resin	Water absorbed (ml./eq.)
A	0.000	183
A	1.000	132
B	0.000	145
B	0.352	133
B	0.402	131
B	0.661	119
B	0.687	119
B	1.000	107

Fig. 2


205
190
175
160
145
130
115
100
0
0.2
0.4
0.6
0.8
1.0
$\frac{\delta V}{n^\circ}$
Resin A
Resin B
NH_4Res

1014.60 g. solution
53.50 g. NH_4Cl
961.10 g. water

Now let all of the ammonium chloride be replaced by hydrochloric acid, as would happen if complete ion exchange occurred.

961.10 g. water
36.47 g. HCl
997.57 g. solution

This solution contains $\frac{36.47}{997.57} \times 100 = 3.756$ % HCl. A solution of this composition has a density of 1.0169; hence there is $\frac{997.57}{1.0169} = 980.99$ ml. of solution/eq. HCl, or 1000-980.99 = 19.01 ml. decrease in volume due to ion exchange has occurred.

Since 50 ml. portions of solution were used for these exchanges, the error in the calculated amount of water absorbed by the resin upon exchange would be approximately $\frac{(19.01)(50)(x)}{1000}$ ml., where x = number of equivalents of ion exchanged. This correction is $\frac{(18.57)(50)(x)}{1000}$ for an exchange beginning with 1 N hydrochloric acid.

The water absorption data of Table 1, after application of this correction, are shown in Table 5, in which they are compared with values obtained by the direct method. In order to obtain more accurate results, four exchanges were carried out on samples of resin which were five times as large, in solutions of the usual volume. If the experimental error were the same the percentage error would be greatly reduced,

Table 5

Corrected Data on Hydrogen-Ammonium Exchange (Resin A)

Initial resin	No. of equivalents of resin used	Mole fraction NH_4 resin at equilibrium	Total water absorbed as calculated from increase in ionic strength of solution (ml./eq.) (corrected)	Total water absorbed (linear interpolation from Table IV ml./eq)
H Res	0.00485	0.000	186	183
NH_4 Res	0.00477	0.262	160	170
H Res	0.00893	0.413	167	162
H Res	0.00867	0.529	194	156
NH_4 Res	0.00741	0.551	161	155
H Res	0.00744	0.644	153	150
NH_4 Res	0.00677	0.647	154	150
NH_4 Res	0.00801	0.746	161	145
H Res	0.00504	0.850	171	139
NH_4 Res	0.00374	1.000	142	132

as all results are calculated on the basis of one equivalent of resin. The results of these exchanges are given in Table 6, in which they are compared with values obtained by the direct method.

From the results of these studies, it can be concluded that the apparent non-equivalence of ion exchange is probably due to three causes: (1) adsorption of electrolyte by the resin, (2) absorption or desorption* of water by the resin, and (3) change in volume of the solution due to exchange of electrolytes of different apparent molal volume.

*Desorption would occur if the initial resin contained more water than the saturated equilibrium resin.

Table 6

Data on Hydrogen-Ammonium Exchange (Resin B)

Initial resin	No. of equivalents of resin used	Mole fraction NH_4 resin at equilibrium	Total water absorbed as calculated from increase in ionic strength of solution (ml./eq., corrected)	Total water absorbed (linear interpolation from Table IV, ml./eq.)
H Res*	0.01548	0.000	149	145
NH_4 Res	0.03693	0.520	126	127
H Res	0.02923	0.678	115	119
NH_4 Res*	0.01764	1.000	109	107

* Since analysis for only one ion was necessary, smaller samples were used.

Silver-Hydrogen Exchange

Since, in their study of the silver-hydrogen exchange, Lowen and Stoenner (6) noted anomalous behavior which they attributed to a considerable adsorption of silver ion by the resin, it was thought that it would be advisable to make a very thorough investigation of this system, in order further to check the conclusions which were reached from a study of the ammonium-hydrogen exchange.

As a preliminary step, the water contents of the pure silver and of the pure hydrogen resin (as used) were determined from the loss in weight upon drying these resins at 110° F., and their total capacity for absorption of water was determined by immersion in water and drying in the manner described previously. The water content of the hydrogen resin as used was found to be 98.7 g., and that of the silver resin 54.8 g., per equivalent of resin. Their maximum water absorption capacities were found to be 142 and 85.5 g. per equivalent, respectively. As there had been found to be a linear relationship between the resin composition and the maximum water absorption capacity for the ammonium and hydrogen resins, a similar relationship was assumed to exist also for the silver and hydrogen resins.

The change in volume of 50 ml. of solution containing originally 0.05 equivalent of nitric acid or of silver nitrate, upon complete exchange of ions, was calculated,

densities being taken from the International Critical Tables. In contrast to the ammonium-hydrogen exchange, the apparent molal volumes of silver nitrate and nitric acid were found to be nearly the same, the average change in volume of this solution being only 0.04 ml. Since complete exchange of ions in solution was never realized in these experiments, the resulting change was so small as to be within the limits of experimental error, and therefore no correction was necessary because of it.

The silver-hydrogen exchange reactions were carried out according to the same procedure as was used for the ammonium- hydrogen exchanges. The initial and final resin compositions, and the quantities of both electrolytes adsorbed were determined experimentally.

In this exchange, as in the previous one, equivalence of exchange was found to occur, in that the capacity of the resin remained unchanged. The results of these exchanges are presented in Tables 7 and 8 and in Figures 3 and 4. The values of K_c are seen to vary regularly from approximately 6 to 19 over the entire range of resin compositions. This may be compared with the values ranging from 5 to 9 which were calculated by Lowen and Stoenner. The large discrepancy in the values of K_c for resins high in silver ion content is probably due to errors in resin composition arising from the calculation (instead of experimental determination) of the quantity of adsorbed electrolyte. The value of the total

Table 7

Silver-Hydrogen Exchange

Initial resin	$N_{Ag\ Res}$ at equilibrium	Capacity of Resin for water Absorption (ml./eq.) Calc. from direct measurement	Calc. from change in ionic strength of solution	$K_c = \frac{(H^+)(Ag\ Res)}{(Ag^+)(H\ Res)}$
H Res	0.932	90	105	12.02
H Res	0.713	102	118	8.47
H Res	0.701	103	119	8.30
H Res	0.538	112	143	7.45
H Res	0.477	116	128	7.12
H Res	0.177	132	137	6.17
H Res	0.000	142	132	-
Ag Res	1.000	86	-	-
Ag Res	0.981	87	97	18.29
Ag Res	0.979	87	99	17.02
Ag Res	0.935	90	98	12.65
Ag Res	0.815	96	97	9.63
Ag Res	0.685	104	102	8.32
Ag Res	0.568	110	105	7.69
Ag Res	0.534	112	105	7.67

Table 8

Adsorption Of Electrolyte On Resin

Initial resin	N_{AgRes} at equilibrium	Equivalents of electrolyte adsorbed by resin			Total equivalents absorbed per equivalent of resin
		HNO_3	$AgNO_3$	Total	
H Res	0.932	0.00074	0.00076	0.00150	0.0609
H Res	0.713	0.00059	0.00012	0.00071	0.0305
H Res	0.701	0.00042	0.00008	0.00050	0.0261
H Res	0.538	0.00035	0.00004	0.00039	0.0213
H Res	0.477	0.00021	0.00002	0.00023	0.0161
H Res	0.177	0.00021	0.00001	0.00022	0.0122
H Res	0.000	0.00017	-	0.00017	0.0098
Ag Res	1.000	-	0.00141	0.00141	0.0909
Ag Res	0.981	0.00037	0.00096	0.00133	0.0800
Ag Res	0.979	0.00047	0.00128	0.00175	0.0767
Ag Res	0.935	0.00047	0.00045	0.00092	0.0565
Ag Res	0.815	0.00048	0.00017	0.00065	0.0373
Ag Res	0.685	0.00036	0.00007	0.00043	0.0271
Ag Res	0.568	0.00030	0.00003	0.00033	0.0210
Ag Res	0.534	0.00028	0.00003	0.00031	0.0232

Fig. 3

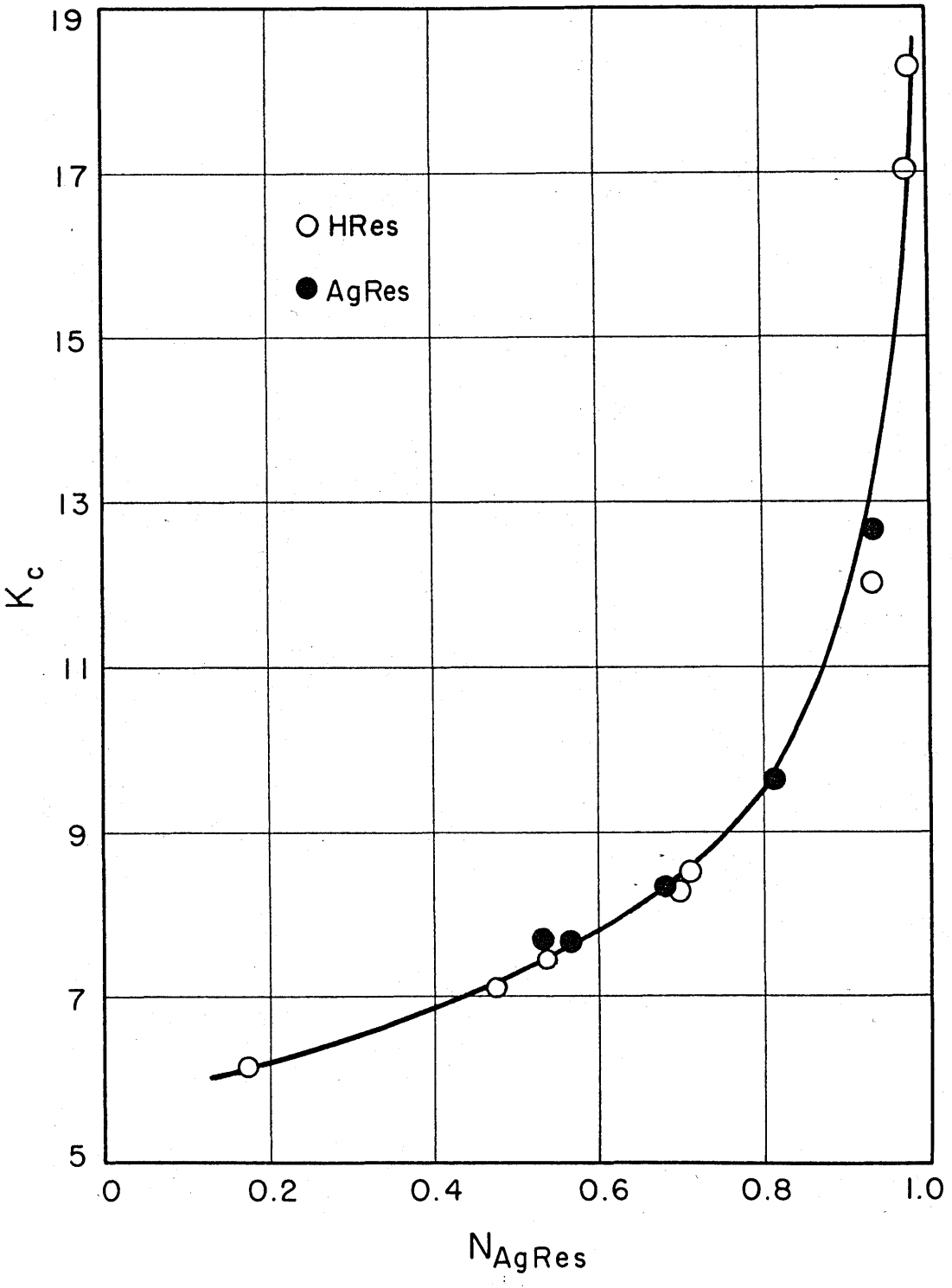
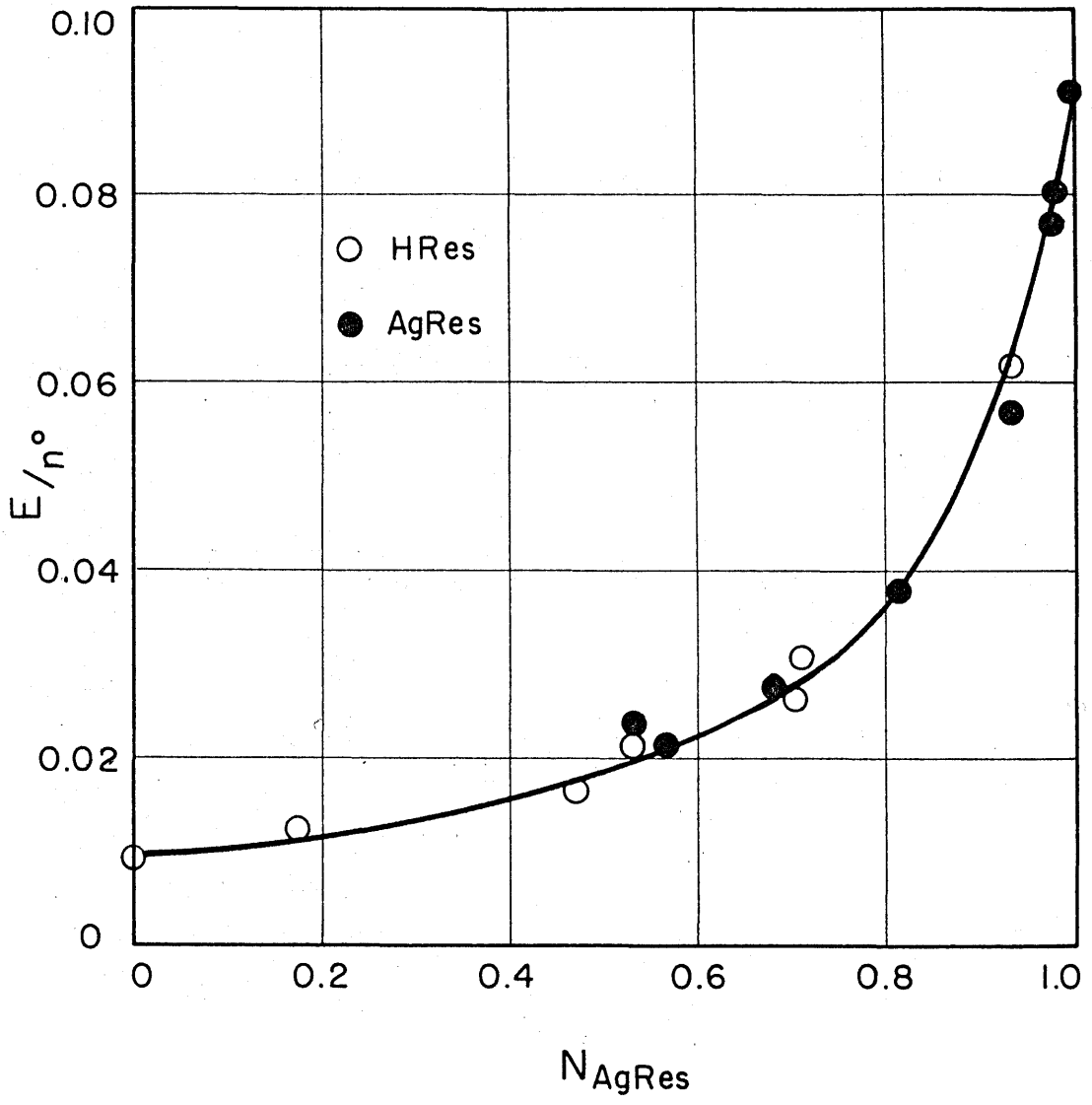


Fig. 4



water uptake by the resin as calculated from the changes in ionic strength of the solution is seen to be in fair agreement with the more nearly correct value as determined directly. The total quantity of electrolyte adsorbed appears to be almost solely a function of the resin composition, the resins high in silver ion having a much greater capacity for adsorption of electrolyte than those high in hydrogen ion content. The quantity of each electrolyte adsorbed is proportional to its concentration in the solution, nitric acid having a slightly greater tendency to be adsorbed than silver nitrate.

The exchange of this pair of ions offers a more severe test than was afforded by previous data of the theory previously advanced to explain the change in ionic strength of the solution upon exchange of ions. In contrast to the results observed in the ammonium-hydrogen exchange, the total ionic strength of the solution <u>decreases</u> in exchanges resulting in a resin high in silver ion content, although it increases in exchanges resulting in a resin high in hydrogen ion content. These facts mean that in the former exchanges the ratio of the number of milligram-equivalents of electrolyte adsorbed to the number of milliliters of water absorbed must be greater than the normality of the initial solution, while in the latter exchanges this ratio must be less than the initial normality. These relationships are shown in Table 9, where it may be seen that the point at which the observed change in ionic strength changes from a

Table 9

Change In Ionic Strength Of Solution Upon Exchange

Initial resin	N_{AgRes} at equilibrium	Total normality of solution Initial	Final	Total mg.-eq. electrolyte adsorbed by resin	Total ml. water absorbed by resin (calcd. from direct measurement)	Ratio mg.-eq./ml.
H Res	0.932	0.9979	0.9556	1.50	-0.22	-
H Res	0.713	0.9765	0.9664	0.71	0.07	10.1
H Res	0.701	0.9573	0.9417	0.50	0.08	6.2
H Res	0.538	0.9677	0.9670	0.39	0.23	1.7
H Res	0.477	0.9590	0.9593	0.23	0.25	0.92
H Res	0.177	0.9612	0.9668	0.22	0.60	0.37
H Res	0.000	0.9614	0.9692	0.17	0.76	0.22
Ag Res	1.000	0.9979	0.9735	1.41	0.49	2.9
Ag Res	0.981	0.9833	0.9669	1.33	0.55	2.5
Ag Res	0.979	0.9833	0.9596	1.75	0.76	2.3
Ag Res	0.935	0.9573	0.9442	0.92	0.59	1.6
Ag Res	0.815	0.9590	0.9625	0.65	0.73	0.89
Ag Res	0.685	0.9612	0.9687	0.43	0.79	0.54
Ag Res	0.568	0.9614	0.9743	0.33	0.88	0.38
Ag Res	0.534	0.9614	0.9706	0.31	0.76	0.41

negative to a positive quantity is in agreement with the point of change predicted from the independent experimental measurements of the adsorption and the water uptake.

Summary

In an attempt to determine the reason for some of the anomalies reported by Lowen and Stoenner (6) two exchange systems involving H^+, NH_4^+, and Ag^+ ions have been studied. It is found that the apparent non-equivalence of exchange is due to the following factors: (1) absorption or desorption of water by the resin; (2) adsorption of ions on the resin; (3) change in volume of the solution due to exchange of electrolytes of differing apparent molal volumes. The equilibrium water absorption is found to be a linear function of resin composition, independent of the initial water content of the resin. Ion adsorption presumably occurs in all exchange systems, but, among those studied, it is by far the greatest in the case of resins of high silver ion content.

Depending upon the relative magnitude of each of the above effects, the ionic strength of the equilibrium solution may be either greater or less than that of the initial solution.

PART II

A STUDY OF ION EXCHANGE EQUILIBRIA

Introduction

Although attempts have been made to formulate heterogeneous cation exchange equilibria in terms both of the Langmuir adsorption mechanism (1) and of the Donnan membrane equilibrium (2), the most fruitful theoretical treatments of such equilibria have been those based upon the application of the law of chemical equilibrium to the exchange, regarded as a simple metathetical reaction (1, 2, 3, 4, 5).

Thus, in the simplest case, when both of the cations are univalent, let us consider the reaction to be that represented by the equation

$$A^+ + BR = AR + B^+$$

where A^+ and B^+ are the cations involved in the exchange and R represents the active anionic portion of the insoluble resin. From a purely thermodynamic viewpoint, then, and regardless of the structure of the resin, the following equation should be applicable:

$$\frac{a_{B^+}\, a_{AR}}{a_{A^+}\, a_{BR}} = K \qquad (1)$$

where a_{A^+}, and a_{B^+} are the activities of the respective ions in the solution and a_{AR} and a_{BR} the activities of the two resin components when equilibrium has been attained, and K, the activity quotient, must by definition be constant at a

fixed temperature regardless of the initial concentrations. This relationship may alternatively be expressed by the equation

$$\frac{c_{B^+}\ \gamma_{B^+}\ a_{AR}}{c_{A^+}\ \gamma_{A^+}\ a_{BR}} = K \qquad (2)$$

where c and γ represent the molarity and the molar activity coefficient of an ion; or better, if the cations are present in solution together with the anion X^-,

$$\frac{c_{B^+}\ \gamma_{\pm}^2{}_{BX}\ a_{AR}}{c_{A^+}\ \gamma_{\pm}^2{}_{AX}\ a_{BR}} = K \qquad (3)$$

where $\gamma_{\pm}$ represents the mean activity coefficient of the electrolyte in question.

If the activity coefficients of the resin components (on a mole fraction basis) are included in the expression for the thermodynamic equilibrium constant, equation (3) becomes

$$\frac{c_{B^+}\ \gamma_{\pm}^2{}_{BX}\ N_{AR} f_{AR}}{c_{A^+}\ \gamma_{\pm}^2{}_{AX}\ N_{BR}\ f_{BR}} = K \qquad (4)$$

An alternate expression which will be used later is

$$\frac{f_{AR}\ K_c'}{f_{BR}} = K \qquad (5)$$

where

$$\frac{c_{B^+}\ \gamma_{\pm}^2{}_{BX}\ N_{AR}}{c_{A^+}\ \gamma_{\pm}^2{}_{AX}\ N_{BR}} = K_c' \qquad (6)$$

Equation (4) contains a total of eight quantities which must be determined experimentally in order to evaluate K. The activity coefficients of the individual electrolytes in mixed solutions are, at least in principle, determinable by experiment, although their actual values are known only in relatively few instances (8). To obviate this difficulty many investigators (1, 2, 5) have used very dilute solutions in order that the activity coefficients might be approximately equal to unity. This choice of procedure, however, probably increased the uncertainty in the experimental values obtained. Others (6, part I) have used the activity coefficients which are available for pure solutions of electrolytes, applying the approximation that they are constant for a given exchange system at a constant total ionic strength. As has been mentioned previously[1], few investigators have determined directly the concentrations of both of the cations in the solution at equilibrium, and, so far as the author's knowledge goes, none has determined experimentally the composition of the resin phase at equilibrium. As has been shown[2], the composition of the equilibrium resin cannot be successfully calculated merely from a knowledge of the change in concentration of one, or even

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1. This Thesis, Part I, page 3.

2. This Thesis, Part I, page 12.

of both, ions in the solution upon exchange. This conclusion follows from the fact that the total ionic strength of the solution changes because of absorption or desorption of water by the resin, adsorption of electrolyte by the resin, and change in volume of the solution due to the exchange of electrolytes of differing apparent molal volumes. In addition, when resins of the Amberlite-IR type are used, the constancy of exchange capacity of the resin cannot always be depended upon as this capacity is a function of the pH of the solution. While, in the more favorable cases, all of the above quantities may be known, no method exists at present for the evaluation of the activity coefficients of the components of the resin phase. The usual assumption (1) is that the resin phase behaves as an ideal solid solution, so that the activity of each of the two components is proportional to its mole fraction. That this assumption, however, is rarely, if ever, valid, is shown by the lack of constancy of the quotient K_c' when a system is carefully studied over a wide range of equilibrium resin compositions. It has been suggested also (9) that the activity coefficients, f, of the resin components ($f = \frac{a}{N}$, where N is the mole fraction of the component in the resin) may vary with composition according to the simplified Margules equations

$$\log f_{AR} = C\, N^2_{BR} \qquad (7)$$

and

$$\log f_{BR} = C\, N^2_{AR} \qquad (8)$$

where C is a constant whose value depends upon the particular combination of resin components under consideration, but is independent of their proportions. Such variation of the activity coefficients with composition is consistent with the Gibbs-Duhem equation for a binary system

$$N_1 \, d \log f_1 + N_2 \, d \log f_2 = 0$$

If now equation (5) is rewritten in logarithmic form as

$$\ln K = \ln K_c' + \ln \frac{f_{AR}}{f_{BR}} \qquad (9)$$

and combined with equations (7) and (8), we find

$$\ln K = \ln K_c' + C(N_{BR}^2 - N_{AR}^2) \qquad (10)$$

Thus a plot of $\ln K_c'$ vs. $(N_{BR}^2 - N_{AR}^2)$ would consist of a straight line of slope -C and intercept ln K. It should be remembered, however, that simplified Margules equations are no more than convenient empirical expressions, having no theoretical significance.

It was the purpose of this research (1) to study ion exchange equilibria as thoroughly as possible, determining experimentally all four quantities appearing in the equilibrium quotient K_c, (2) to combine these data with activity data for mixed solutions of electrolytes as found in the literature (8), and (3) to determine, if possible, the true value of the equilibrium constant K in each case.

Experimental Methods

General Method---For the study of the sodium-hydrogen exchange reaction, two "pure" resins were prepared, one containing each of the cations involved in the exchange. The exchange reactions were carried out according to the same procedure as has been described previously.[3] The nature of the exchange process having already been determined, however, no further absorption or adsorption data were required. Hence, only the final solution concentrations and final resin compositions were determined experimentally. The exchange was studied over a wide range of equilibrium resin compositions, the ionic strength of the solution being maintained approximately constant, in one series of experiments at 1 molar and in another series at 0.3 molar.

Hydrogen Resin---The hydrogen resin which had been prepared for use in the studies reported in Part I was used also in this work.

Sodium Resin---The pure sodium resin was obtained by maintaining a portion of the hydrogen form in contact with a large excess of saturated sodium chloride solution for two hours; during this time, sodium hydroxide solution was intermittently added to bring the pH of the solution up to that of a saturated sodium chloride solution, where it eventually remained constant. The product was then washed

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3. This Thesis, Part I, page 7.

and dried in the manner described for the hydrogen resin.

Equilibrium Resin---The equilibrium resin was washed, air-dried, and separated into two samples of known weight. On one sample, the hydrogen ion was determined by addition of a concentrated solution of sodium chloride and titration with standard sodium-hydroxide solution. The other sample was placed in a micro-exchange column and the sodium ion was completely replaced by passage of 6M hydrochloric acid through the column until the effluent gave a negative test for sodium ion. The combined effluent solutions were evaporated, transferred to a 100 ml. volumetric flask, and diluted to volume. Aliquot portions were then evaporated to dryness and ignited, and the residues were weighed directly as sodium chloride (10). The concentration of sodium ion in equilibrium solutions was determined in the same manner. The solution concentrations are calculated as equivalents of ion per liter of solution. The resin composition is calculated as equivalents of ion per gram of air-dried resin.

Theoretical Considerations

Although the experimental evaluation of the activities in the resin phase constitutes a problem of great difficulty, a method has been devised by means of which they may be calculated. The constancy of K, as defined in equations (1) through (5), is a thermodynamic necessity, consequent upon the definition of activities and upon the formulation of the process, and independent of the mechanism or the nature of the solid phase. Hence, the application of the law of chemical equilibrium furnishes a relationship which may be combined with the Gibbs-Duhem equation in such a manner that, in cases where the activity coefficients in the solution are known, both the true equilibrium constant and the activity coefficients in the solid phase may be determined from the experimental data.

Let the exchange reaction be represented by the equation

$$A^{+} + BR = AR + B^{+}$$

in which case equations (1) through (6) are valid. If now subscript 1 refers to AR and subscript 2 refers to BR, equation (5) leads to the logarithmic relation

$$\ln K = \ln K_c' + \ln f_1 - \ln f_2 \qquad (11)$$

and differentiating both sides of this equation, meanwhile recognizing that K, the true thermodynamic equilibrium constant, is necessarily constant, we obtain the result

$$d \ln f_1 - d \ln f_2 = -d \ln K_c' \qquad (12)$$

The Gibbs-Duhem equation for the two components of this binary solid solution is

$$N_1 \, d \ln f_1 + N_2 \, d \ln f_2 = 0 \qquad (13)$$

Equations (12) and (13) may be solved with the following results:

$$d \ln f_1 = -N_2 \, d \ln K'_c \qquad (14)$$

and

$$d \ln f_2 = N_1 \, d \ln K'_c \qquad (15)$$

Noting that $\ln f_1 = 0$ at $N_2 = 0$, and $\ln f_2 = 0$ at $N_1 = 0$, we may integrate by parts and evaluate $\ln f_1$ and $\ln f_2$ as follows:

$$\ln f_1 = \int_{N_2=0}^{N_2=N_2} -N_2 \, d \ln K'_c = -N_2 \ln K'_c \Big]_{N_2=0}^{N_2=N_2} + \int_0^{N_2} \ln K'_c \, dN_2$$

$$= -N_2 \ln K + \int_{N_1}^{1} \ln K'_c \, dN_1 \qquad (16)$$

$$\text{and } \ln f_2 = \int_{N_1=0}^{N_1=N_1} N_1 \, d \ln K'_c = N_1 \ln K'_c \Big]_{N_1=0}^{N_1=N_1} - \int_0^{N_1} \ln K'_c \, dN_1$$

$$= N_1 \ln K'_c - \int_0^{N_1} \ln K'_c \, dN_1 \qquad (17)$$

These results may be substituted in Equation (11) to obtain the value of the true equilibrium constant, as follows:

$$\ln K = \ln K_c' - N_2 \ln K_c' + \int_{N_1}^{1} \ln K_c' \, dN_1 - N_1 \ln K_c'$$

$$+ \int_{0}^{N_1} \ln K_c' \, dN_1 = \int_{0}^{1} \ln K_c' \, dN_1 \qquad (18)$$

It is thus apparent that from a plot of log K_c' against the resin composition N_1, the activity coefficients f_1 and f_2, as well as the equilibrium constant K, corresponding to any value of K_c, may all be determined by graphical integration.

It may be noted that the activity coefficient and equilibrium constant treatment outlined above for a simple uni-univalent exchange may be generalized to include exchange between electrolytes of different valence types. In such cases it is necessary merely to replace the integration variable N, by the generalized variable $X = \frac{Z_1 N_1}{(Z_1 - Z_2)N_1 + Z_2}$, Z_1 and Z_2 being the valences of the exchanging ions. Thus for the exchange

$$Z_2 A^{Z_1+} + Z_1 B R_{Z_2} = Z_1 B^{Z_2+} + Z_2 A R_{Z_1}$$

we obtain the results

$$-Z_2 \ln f_1 = (1-X) \ln K_c' - \int_{X}^{1} \ln K_c' \, dX \qquad (19)$$

$$-Z_1 \ln f_2 = -X \ln K'_c + \int_0^X \ln K'_c \, dX \qquad (20)$$

$$\ln K = \int_0^1 \ln K'_c \, dX \qquad (21)$$

Sodium-Hydrogen Exchange

Harned and Owen (8) have shown that in some cases there is a linear relationship between the logarithm of the mean activity coefficient of an electrolyte in a binary solution of electrolytes at constant total ionic strength, and the individual concentration of that electrolyte in the mixed solution. The equations to express this relationship are

$$\log \gamma_1 = \log \gamma_{1(0)} - \alpha_{12} \mu_2 \qquad (22)$$

and

$$\log \gamma_2 = \log \gamma_{2(0)} - \alpha_{21} \mu_1 \qquad (23)$$

where $\gamma_{1(0)}$ and $\gamma_{2(0)}$ are the mean activity coefficients, respectively, of the electrolytes in their own pure solution, and α_{12} and α_{21} are constants for mixtures of the particular electrolytes in question at the given total ionic strength. When those quantities with subscript 1 refer to hydrochloric acid and those with subscript 2 to sodium chloride, the following data are given for a solution of total ionic strength equal to one molal:

$\alpha_{12} = +0.032$

$\alpha_{21} = -0.058$

$\gamma_{1(0)} = 0.809$ in 1 molal solution of pure HCl

$\gamma_{2(0)} = 0.658$ in 1 molal solution of pure NaCl

Likewise for a solution of total ionic strength equal to 0.3 molal the following data are given:

$\alpha_{12} = +0.038$

$\alpha_{21} = -0.057$

$\gamma_{1(0)} = 0.757$ in 0.3 molal solution of pure HCl

$\gamma_{2(0)} = 0.710$ in 0.3 molal solution of pure NaCl

It is evident that, in each case, K_c' may be calculated from the results of an experimental determination of the concentration of each cation in the equilibrium solution and the composition of the resin phase at equilibrium, together with the activity coefficients calculated from the above data of Harned and Owen. Such data and calculations, for exchanges in which the total ionic strength of the equilibrium solution was approximately 1 molar, are shown in Table 10. In Table 11 are presented similar results for exchanges in which the resulting solution at equilibrium was approximately 0.3 molar. The calculated values of K_c', resulting from both series of exchange reactions, are plotted as a function of resin composition in Figure 5. From this plot, by means of graphical integration, the value of the equilibrium constant, K, and the values of the activity coefficients of each of the components of the resin phase may be obtained. The value of

$$K = \frac{a_{HCl}\, a_{NaRes}}{a_{NaCl}\, a_{HRes}}$$

as calculated from the results of the exchanges in which the ionic strength of the solution was 1 molar, was found to be 1.73, while its value, as calculated from the results of ex-

Table 10

Sodium-Hydrogen Exchange (1)

Initial resin	$N_{Na\ Res}$	Concentration at equilibrium		$\log \gamma_{HCl}$	$\log \gamma_{NaCl}$	K_c	K'_c
		HCl	NaCl				
H Res	0.184	0.8453	0.1116	-0.0970	-0.1302	1.71	1.99
H Res	0.336	0.7395	0.2243	-0.1005	-0.1370	1.67	1.98
H Res	0.485	0.6079	0.3603	-0.1048	-0.1450	1.58	1.90
H Res	0.588	0.4941	0.4849	-0.1082	-0.1520	1.46	1.79
H Res	0.702	0.3616	0.6281	-0.1125	-0.1603	1.35	1.68
H Res	0.795	0.2324	0.7619	-0.1168	-0.1680	1.18	1.49
Na Res	0.327	0.7333	0.2179	-0.1009	-0.1368	1.65	1.95
Na Res	0.483	0.6417	0.3562	-0.1045	-0.1448	1.61	1.94
Na Res	0.588	0.5028	0.4739	-0.1080	-0.1515	1.51	1.85
Na Res	0.698	0.3662	0.6182	-0.1122	-0.1600	1.37	1.71
Na Res	0.796	0.2372	0.7571	-0.1164	-0.1680	1.22	1.55
Na Res	0.883	0.1179	0.8855	-0.1201	-0.1751	1.01	1.30
Na Res	0.935	0.0591	0.9459	-0.1221	-0.1790	0.89	1.16

Fig. 5

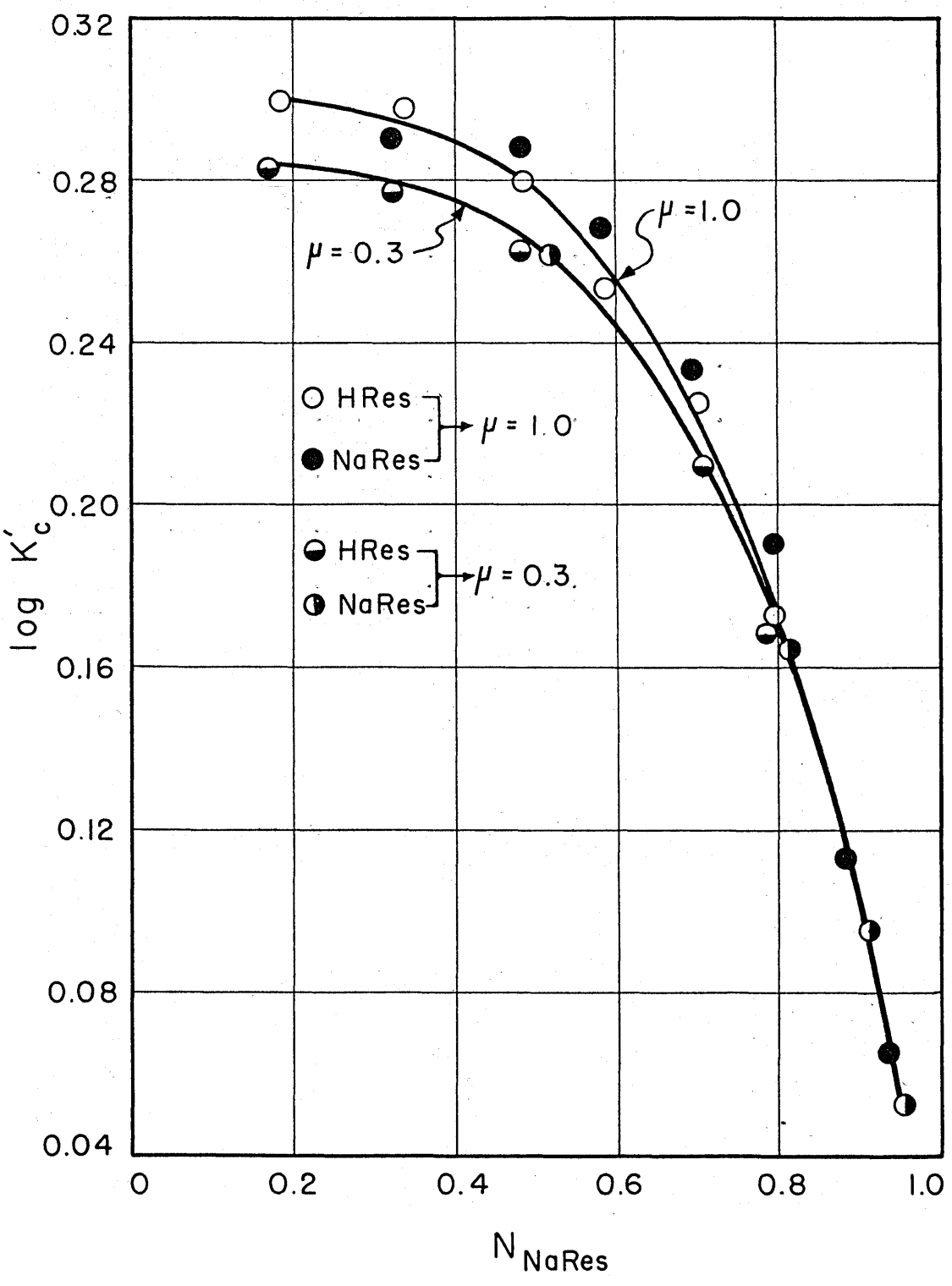

0.32
0.28
0.24
0.20
0.16
0.12
0.08
0.04
log K'c
0
0.2
0.4
0.6
0.8
1.0
N NaRes
μ = 0.3
μ = 1.0
HRes
NaRes
μ = 1.0
HRes
NaRes
μ = 0.3

Table 11

Sodium-Hydrogen Exchange (2)

Initial resin	$N_{Na\ Res}$	Concentration at equilibrium		$\log \gamma_{HCl}$	$\log \gamma_{NaCl}$	K_c	K'_c
		HCl	NaCl				
H Res	0.181	0.2586	0.0315	-0.1226	-0.1337	1.81	1.91
H Res	0.358	0.2253	0.0700	-0.1238	-0.1359	1.79	1.89
H Res	0.482	0.1900	0.1021	-0.1251	-0.1378	1.73	1.84
H Res	0.700	0.1162	0.1784	-0.1278	-0.1421	1.52	1.62
H Res	0.787	0.0820	0.2198	-0.1291	-0.1444	1.37	1.47
Na Res	0.514	0.1808	0.1105	-0.1254	-0.1382	1.72	1.83
Na Res	0.805	0.0753	0.2271	-0.1293	-0.1448	1.36	1.46
Na Res	0.900	0.0343	0.2642	-0.1308	-0.1470	1.16	1.25
Na Res	0.960	0.0125	0.2910	-0.1316	-0.1485	1.03	1.11

changes in which the ionic strength of the solution was 0.3 molar, was found to be 1.68. The values of the activity coefficients at various resin compositions are given in Table 12.

From the theoretical point of view, the values of the equilibrium constant and of the activity coefficients of each of the components of the resin phase should be independent of the ionic strength of the external solution. Therefore the small discrepancies which are noted must be due to experimental error. There are several possible sources of error. In the first place, the activity coefficients of hydrochloric acid in the aqueous phase were not experimentally determined over the entire range of compositions. Also the activity coefficients of sodium chloride were not determined directly, but were calculated in a somewhat indirect manner. Although it is believed that little error is present in the experimentally determined values of the hydrogen ion concentration in the solution and resin phases, there is a possibility of greater error in the sodium ion analyses. Even so, the disagreement in the values of the equilibrium constant is not great, and the agreement between the calculated values of the activity coefficients is excellent except in the cases of resins containing small quantities of the ion in question, in which cases the calculated values were necessarily obtained from extrapolated portions of the curve.

Table 12

Activity Coefficients of Sodium Resin and Hydrogen Resin at Various Resin Compositions

	= 1.0		= 0.3	
$N_{Na\ Res}$	$f_{Na\ Res}$	$f_{H\ Res}$	$f_{Na\ Res}$	$f_{H\ Res}$
0.0	0.865*	1.000	0.879*	1.000
0.1	0.867	0.999	0.879	1.000
0.2	0.870	0.999	0.879	1.000
0.3	0.876	0.996	0.883	0.997
0.4	0.884	0.992	0.887	0.995
0.5	0.894	0.983	0.899	0.984
0.6	0.909	0.963	0.917	0.960
0.7	0.933	0.916	0.940	0.917
0.8	0.964	0.836	0.966	0.847
0.9	0.986	0.720	0.989	0.735
1.0	1.000	0.532*	1.000	0.583*

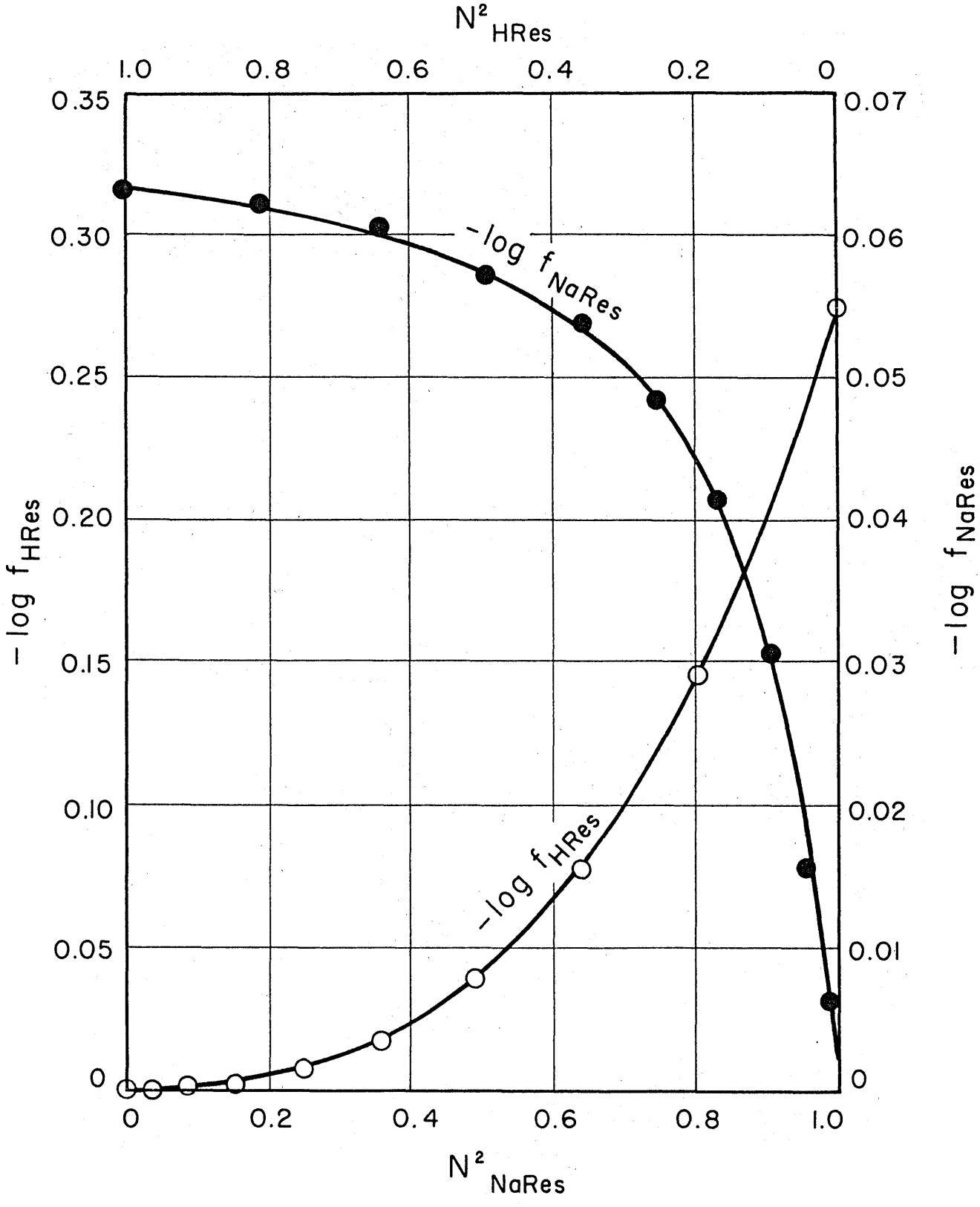
* Extrapolated values

It is of interest to note that the evaluation of these activity coefficients cannot be accomplished by the use of simple relationships between them and the resin composition, such as, for example, are indicated by the empirical Duhem-Margules equations

$$\log f_1 = CN_2^2 \text{ and } \log f_2 = CN_1^2$$

When, with values calculated from exchanges in which the ionic strength of the aqueous solution was approximately 1 molar, $\log f_1$ is plotted vs. N_2^2 and $\log f_2$ is plotted vs. N_1^2, there is considerable deviation from linearity, as is shown in Figure 6.

Fig. 6


N^2_{HRes}
1.0
0.8
0.6
0.4
0.2
0
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
$-\log f_{NaRes}$
$-\log f_{HRes}$
$-\log f_{HRes}$
$-\log f_{NaRes}$
0
0.2
0.4
0.6
0.8
1.0
N^2_{NaRes}

Summary

The sodium-hydrogen exchange system has been studied with Dowex-50 as exchanger over a wide range of equilibrium resin compositions in solutions of constant total ionic strength of (1) approximately 1 molar and (2) approximately 0.3 molar. In this system the apparent equilibrium constant K'_c was found to vary regularly with equilibrium resin composition, this variation indicating that the usual assumption of ideal solid solution behavior in the exchanger phase must be invalid. Exchange data have been combined with activity coefficient data from the literature for a more accurate interpretation of this system. A new method has been devised for the determination by graphical means of the resin phase activity coefficients and the true thermodynamic equilibrium constant in an exchange system. A single term Margules expansion of the activity coefficients was found not to be applicable in the case of the sodium-hydrogen exchange.

PART III

THE DETERMINATION OF ACTIVITY COEFFICIENT RATIOS OF NITRIC ACID AND SILVER NITRATE IN BINARY AQUEOUS SOLUTIONS, AND THEIR APPLICATION TO ION EXCHANGE EQUILIBRIA

Introduction

In the ion exchange work which was reported in Part II of this thesis, a method was developed by means of which it was possible to calculate the value of the true equilibrium constant for the sodium-hydrogen exchange, as well as the activity coefficients of each of the components of the resin phase throughout the entire composition range. A knowledge of the activity coefficients of nitric acid and silver nitrate, or rather of the ratio of these activity coefficients, in binary aqueous solutions of total ionic strength equal to unity, when combined with the exchange data presented in Part I, would permit a similar treatment of the silver-hydrogen exchange.

Activity coefficient data for this pair of electrolytes over a range of concentrations would also be of intrinsic interest, as it is known that in pure aqueous solutions the value of the activity coefficient of silver nitrate decreases much more rapidly with concentration than does that of nitric acid. This pair of electrolytes would thus probably furnish a test of the ionic strength principle more severe than that

offered by a binary solution of hydrochloric acid and one of the alkali metal chlorides (8), for which case the electrolytes in their pure solutions exhibit more nearly the same dependence of activity coefficient upon concentration.

From a purely thermodynamic point of view, it would seem possible to obtain the value of the ratio of the activity coefficients of nitric acid and silver nitrate, in any solution, from electromotive force measurements on a cell of the type

$$Pt,\ H_2,\ HNO_3(m_1),\ AgNO_3(m_2),\ Ag.$$

Experimentally, however, it is found that silver ion is reduced by the bubbling hydrogen, so that silver plates out on the platinum (hydrogen) electrode, giving erroneous results. If, instead of a hydrogen electrode, a glass electrode, which is unaffected by the presence of easily reducible substances in the solution, is used to indicate the hydrogen activity, data of the desired type may be obtained.

It is true that the use of the glass electrode is accompanied by a certain amount of inconvenience, since the high resistance (10^7 or 10^8 ohms) of the glass membrane necessitates the use either of a current amplification device or of a very sensitive current-detecting device such as the electroscope. Further, since this electrode

does not behave as a perfect hydrogen electrode in all solutions, it must be calibrated before use. The difficulty arising from the high resistance of the electrode is more easily obviated by virtue of the fact that modern thermionic amplifiers are able to amplify a current of 10^{-12} ampere to such an extent that, when an enclosed galvanometer of reasonable sensitivity is used, the potential may be measured with an accuracy of 0.1 millivolt. The deviation of the glass electrode from ideal behavior, however, presents a greater problem, since a completely satisfactory explanation of its cause has not been found. There is considerable evidence (11, 12, 13, 14) that this deviation is greater in solutions of very low or very high pH, and in non-aqueous solutions. The error which is observed in the measurement of the pH of very acid solutions is called the "acid error", and that observed in the measurement of the pH of alkaline solutions is called the "salt error". Dole (12) has attempted, with some success, to correlate all errors in measured pH values with the activity of the water in the solution. It has been found that the "acid error" is not constant for all electrodes, although for each electrode studied it is a function of the hydrogen ion concentration of the solution. For this reason, correction factors which are found in the literature are not applicable to all electrodes; each electrode must be calibrated before use.

Another complicating factor which must be considered is the so called "asymmetry potential". This is the potential across the glass membrane which exists when the solutions and electrodes on each side are identical. Since this potential is not constant but changes slowly with time, its value must be determined frequently. This may be done by direct experimental measurement; or, alternatively, the E^{o} value for the glass electrode may be calculated by comparison of this electrode with another which behaves ideally, and the constant thus obtained will contain all of the necessary correction factors.

In order to use the glass electrode for the purpose of determining the desired activity coefficient ratios, it was necessary to determine a calibration curve for the glass electrode. After many unsuccessful attempts to arrive at a semi-permanent curve, it was found that the glass electrode must be calibrated twice daily or before each period of continual use. Because of the anomalous behavior which was noted in some of the calibration attempts, it was decided that some time should also be devoted to a study of the characteristics of the glass electrode and the causes of its deviation from ideal behavior.

Experimental Methods

Silver Electrode---The silver electrodes which were used in these experiments were prepared either by a thermal or by an electrolytic method. In the former case, a paste of freshly prepared silver oxide was placed on a platinum wire which had been cleaned with nitric acid, and was thermally decomposed by heating at 400° C. for 10 minutes. After preparation, the electrodes were thoroughly washed first with dilute nitric acid and then with distilled water. In the latter case, the electrodes were prepared by the rapid electrolysis of a solution of silver nitrate which had been acidified with a little nitric acid, and were washed as before. The standard potentials of all of the electrodes, prepared by either method, were checked in the manner described below, and those which were in error by more than 0.4 mv. were rejected. All electrodes were stored in distilled water when not in use. Massive silver electrodes, in contrast with these in which the silver was finely divided, were found in all cases to be unsatisfactory (15).

Silver Chloride Electrode---The silver chloride electrode, in spite of its convenience of form and ease of preparation, has until recently been accepted only with reservations because the standard potential of any given electrode appeared to be somewhat dependent upon the method of preparation of the electrode, and was not in all cases reproducible. Smith and

Taylor (16) have found, however, that with the use of proper care in the preparation of the electrodes, and the allowance of a sufficient period for aging, electrodes prepared either by the thermal, the thermal-electrolytic or the electrolytic method will produce results which are in agreement within 0.02 millivolt. The period required for aging is dependent upon the porosity of the electrode, and may be as long as 20 days. The thermally prepared electrodes appear to reach an equilibrium value in the shortest period of time. The electrodes which were used in this work were either of the thermal or the electrolytic type. The thermal type electrodes (17, 18) were prepared by the thermal decomposition, on a platinum wire, of a paste consisting of seven parts of silver oxide to one part of silver chlorate. This decomposition was accomplished by heating the mixture in an electric furnace at 650° C. for 7 or 8 minutes. The electrolytic type electrodes were prepared by a procedure similar to that of Shedlovsky and MacInnes (19). A fresh coating of silver was deposited on a small piece of silver foil by electrolysis of a solution of silver cyanide at 4 ma. for a period of 24 hours. The electrode was rinsed briefly in concentrated ammonia and then in water for 4 or 5 hours. A dilute solution (approximately 0.1 M) of hydrochloric acid was electrolyzed for one hour at 4 to 6 ma., with this electrode as anode. The electrode was then rinsed for a

period of 24 hours in distilled water. All silver chloride electrodes were stored in a solution of approximately 0.1 N hydrochloric acid, and rinsed thoroughly before use.

Glass Electrode---The glass electrode bulbs were of the low resistance type furnished by Leeds and Northrup. Before use, each bulb was conditioned by soaking in 6 M hydrochloric acid for 2 hours and rinsing with dilute ammonia and distilled water. The platinum inner element supplied with this type of bulb was designed for use with a quinhydrone-hydrochloric acid solution. However, because of the instability of quinhydrone solutions, which necessitates their renewal at frequent intervals, it was found advisable to convert the inner element from a platinum to a silver chloride electrode by the electrolytic method described above. The bulb was then filled with approximately 0.2 M hydrochloric acid, and the electrode was assembled with the silver chloride element inside. The glass electrode was stored in distilled water between periods of use, except in the case of the experiments in which the cause of its deviation from ideal behavior was being investigated.

Auxiliary Apparatus---A Leeds and Northrup thermionic amplifier having a practical limit of sensitivity of 0.1 mv. was used in order that a detectable current might be obtained when the potentiometer was off balance. The galvanometer used was the 2430 type supplied by Leeds and Northrup, with

a sensitivity of 5 x 10^{-4} microampere per millimeter. A standard Leeds and Northrup type K-2 potentiometer was used for electromotive force measurements.

General Methods---Before each series of determinations, the batteries which served as the source of power for the amplifier were allowed to discharge for at least one hour, in order to minimize the drift in the null point of the instrument. In order that an accuracy of 0.1 mv. in the e. m. f. data might be attained, it was necessary, because of the extremely large temperature coefficient of the silver electrode, to maintain the solutions under consideration at a temperature of 25.0 $\pm$ 0.1° C. The potentials of the silver and silver chloride electrodes were found to be dependent upon the depth of immersion; hence, in order to obtain reproducible results, complete immersion was necessary. So long as the bulb was completely immersed, the glass electrode was found to operate properly.

The calibration of the glass electrode at various acid concentrations was carried out by means of the cell

Ag, AgCl, HCl(0.2M), glass, HCl (m), AgCl, Ag.

The activity coefficients of the various hydrochloric acid solutions were interpolated from those given by Harned and Owen (8). The E° value for the glass electrode at any acid concentration was then calculated from the Nernst equation. These E° values were found to change slowly with time, proba-

bly due to a variation in the "asymmetry potential" of the electrode, which will be discussed later in this thesis. On this account, it was necessary to calibrate the electrode before each period of continual use. For the electrode which was to be used in nitric acid-silver nitrate solutions, the E° value, although constant for a given series of experiments, was found to be slightly more positive in 1 M hydrochloric acid than in dilute solutions of the same acid. This "acid error", which also will be discussed later, was found to decrease from 2.8 to 1.8 mv. as the electrode aged. Calibration curves for two typical electrodes are shown in Figure 7.

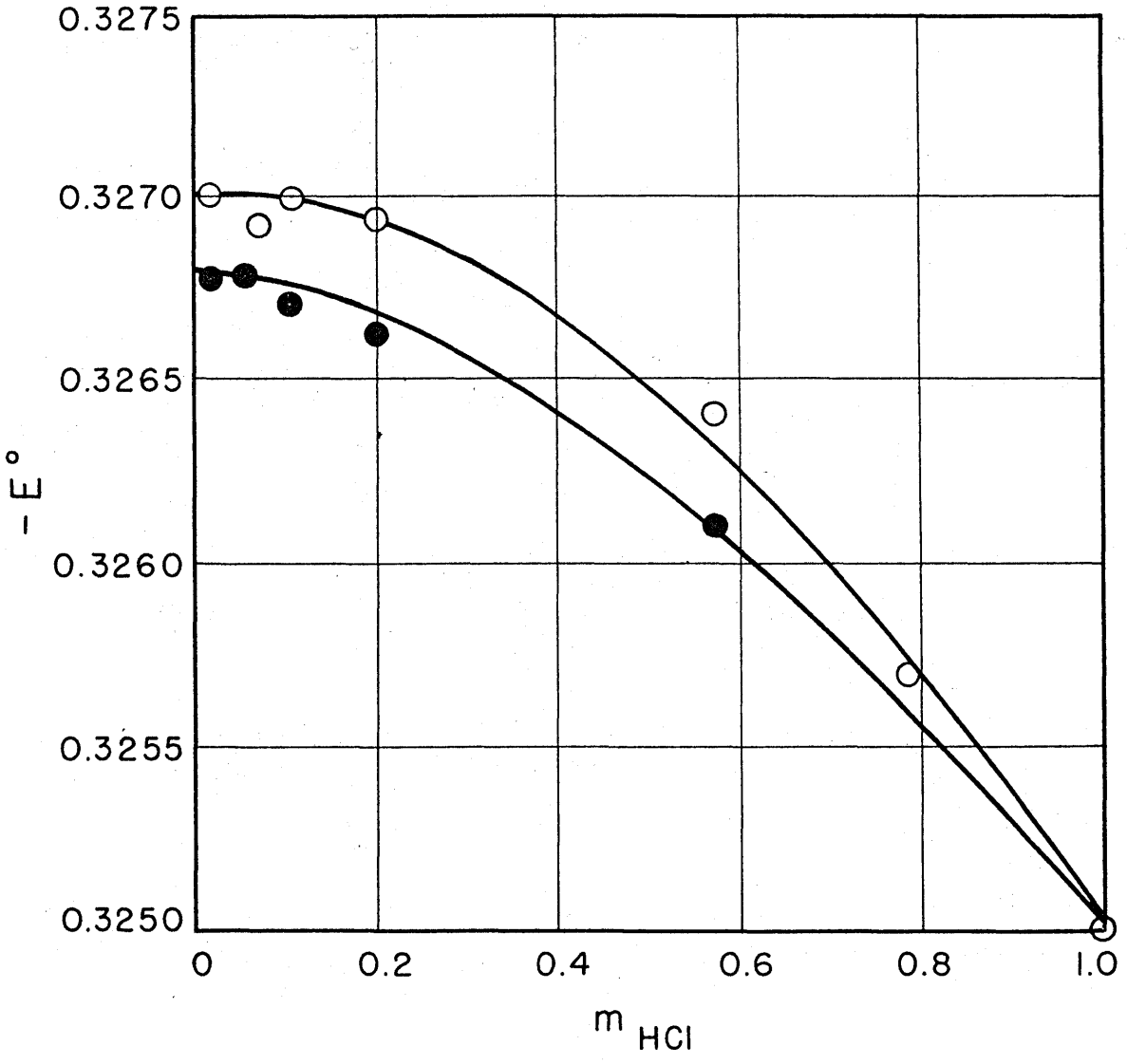
Since the mean activity coefficients of nitric and hydrochloric acids are not greatly different, it was assumed that the glass electrode would function similarly in solutions of either acid, provided that they were no more concentrated than 1 molal. Any error resulting from this assumption would appear only in the more acid solutions, and even there it should be but little greater than the experimental error.

As a check on the standard potential of the silver electrodes used, e. m. f. measurements were made on cells of the type

Ag, AgCl, HCl(0.2M), glass, $HNO_3(m_1)$, $AgNO_3(m_1)$, Ag

where m_1 had values ranging from 0.1 to 0.005 M. An extrapolation to infinite dilution ($m_1 = 0$) should give the value

Fig. 7



of (E° glass - $E^{\circ}Ag$). Silver electrodes whose E° value differed by more than 0.4 mv. from the accepted figure of 0.7995 volt were rejected.

Results

For the cell

Ag, AgCl, HCl(0.2M), glass, $HNO_3(m_1)$, $AgNO_3(m_2)$, Ag

the Nernst equation takes the form

$$E = E^o - \frac{RT}{F} \ln \frac{a_{HNO_3}}{a_{AgNO_3}}$$

or $$E = E^o - \frac{RT}{F} \ln \frac{m_{HNO_3}}{m_{AgNO_3}} - \frac{2RT}{F} \ln \frac{\gamma_{HNO_3}}{\gamma_{AgNO_3}}$$

If the value of E^o is corrected by calibration of the glass electrode, the value of $\gamma_{HNO_3}/\gamma_{AgNO_3}$ may be calculated, for any solution, from the experimental value of E. Such values of E have been determined for various nitric acid-silver nitrate ratios at constant total ionic strengths of 1.0, 0.5, 0.2 and 0.1 molal. These data for three different silver electrodes, together with the calculated activity coefficient ratios, are presented in Tables 13 through 20. Electrodes I and II, as they are designated in these tables, were prepared by the electrolytic method; electrode III was prepared by the thermal method. The mean values for the ratio $\gamma_{HNO_3}/\gamma_{AgNO_3}$ are believed to be accurate to within 0.5%. At any one ionic strength, however, this ratio is found not to be constant, but to vary in a regular manner with the ratio of nitric acid to silver nitrate. This variation is greatly reduced for the more dilute solutions, a fact which indicates that the ionic strength principle may be applied to these solutions with less

Table 13

Electromotive Force Measurements of the Cells

Ag, AgCl, HCl(0.2M), glass, $HNO_3(m_1)$, $AgNO_3(m_2)$, Ag

at Total Ionic Strength of 1.0 Molal

		Electrode I		Electrode II		Electrode III	
m_{HNO_3}	m_{AgNO_3}	E^o	E	E^o	E	E^o	E
0.950	0.050	0.4746	0.3853	0.4745	0.3855	0.4741	0.3846
0.875	0.125	0.4744	0.4098	0.4743	0.4099	0.4739	0.4092
0.750	0.250	0.4740	0.4308	0.4739	0.4308	0.4736	0.4304
0.625	0.375	0.4736	0.4455	0.4735	0.4454	0.4733	0.4450
0.500	0.500	0.4733	0.4581	0.4732	0.4580	0.4731	0.4575
0.375	0.625	0.4731	0.4708	0.4730	0.4705	0.4729	0.4702
0.250	0.750	0.4729	0.4855	0.4728	0.4853	0.4727	0.4850
0.125	0.875	0.4728	0.5068	0.4727	0.5066	0.4726	0.5064
0.050	0.950	0.4728	0.5319	0.4727	0.5318	0.4725	0.5316

Table 14

Values of $\gamma_{HNO_3} / \gamma_{AgNO_3}$ Calculated from Table 13

m_{HNO_3}	m_{AgNO_3}	$\gamma_{HNO_3} / \gamma_{AgNO_3}$			
		I	II	III	Mean
0.950	0.050	1.306	1.298	1.311	1.305
0.875	0.125	1.329	1.323	1.332	1.328
0.750	0.250	1.339	1.336	1.339	1.338
0.625	0.375	1.339	1.339	1.344	1.341
0.500	0.500	1.344	1.344	1.350	1.346
0.375	0.625	1.350	1.350	1.360	1.353
0.250	0.750	1.355	1.357	1.363	1.358
0.125	0.875	1.365	1.368	1.371	1.368
0.050	0.950	1.378	1.378	1.378	1.378

Table 15

Electromotive Force Measurements of the Cells

Ag, AgCl, HCl(0.2M), glass, $HNO_3(m_1)$, $AgNO_3(m_2)$, Ag

at Total Ionic Strength of 0.5 M

		Electrode I		Electrode II		Electrode III	
m_{HNO_3}	m_{AgNO_3}	E^o	E	E^o	E	E^o	E
0.4750	0.0250	0.4731	0.3900	0.4728	0.3895	0.4729	0.3897
0.4375	0.0625	0.4730	0.4151	0.4727	0.4146	0.4728	0.4149
0.3750	0.1250	0.4730	0.4365	0.4727	0.4360	0.4728	0.4364
0.3125	0.1875	0.4729	0.4512	0.4726	0.4508	0.4727	0.4511
0.2500	0.2500	0.4728	0.4641	0.4725	0.4636	0.4726	0.4640
0.1875	0.3125	0.4728	0.4768	0.4725	0.4763	0.4726	0.4769
0.1250	0.3750	0.4727	0.4916	0.4724	0.4912	0.4725	0.4916
0.0625	0.4375	0.4726	0.5133	0.4723	0.5128	0.4724	0.5132
0.0250	0.4750	0.4726	0.5387	0.4723	0.5383	0.4724	0.5386

Table 16

Values of $\gamma_{HNO_3} / \gamma_{Ag\ NO_3}$ Calculated from Table 15

m_{HNO_3}	m_{AgNO_3}	$\gamma_{HNO_3} / \gamma_{Ag\ NO_3}$			
		I	II	III	Mean
0.4750	0.0250	1.157	1.162	1.159	1.159
0.4375	0.0625	1.166	1.171	1.166	1.168
0.3750	0.1250	1.175	1.180	1.173	1.176
0.3125	0.1875	1.182	1.184	1.180	1.182
0.2500	0.2500	1.184	1.189	1.182	1.185
0.1875	0.3125	1.194	1.198	1.187	1.193
0.1250	0.3750	1.198	1.201	1.194	1.198
0.0625	0.4375	1.198	1.203	1.196	1.199
0.0250	0.4750	1.203	1.206	1.201	1.203

Table 17

Electromotive Force Measurements of the Cells

Ag, AgCl, HCl(0.2M), glass, $HNO_3(m_1)$, $AgNO_3(m_2)$, Ag

at Total Ionic Strength of 0.2 M

		Electrode I		Electrode II		Electrode III	
m_{HNO_3}	m_{AgNO_3}	E^o	E	E^o	E	E^o	E
0.1900	0.0100	0.4727	0.3927	0.4723	0.3923	0.4721	0.3922
0.1750	0.0250	0.4726	0.4181	0.4722	0.4177	0.4721	0.4176
0.1500	0.0500	0.4725	0.4397	0.4721	0.4393	0.4721	0.4391
0.1250	0.0750	0.4725	0.4547	0.4721	0.4543	0.4720	0.4541
0.1000	0.1000	0.4725	0.4678	0.4721	0.4674	0.4720	0.4672
0.0750	0.1250	0.4724	0.4808	0.4720	0.4804	0.4719	0.4802
0.0500	0.1500	0.4724	0.4957	0.4720	0.4954	0.4719	0.4952
0.0250	0.1750	0.4724	0.5174	0.4720	0.5172	0.4719	0.5170
0.0100	0.1900	0.4724	0.5431	0.4720	0.5427	0.4719	0.5425

Table 18

Values of $\gamma_{HNO_3}/\gamma_{AgNO_3}$ Calculated from Table 17

m_{HNO_3}	m_{AgNO_3}	$\gamma_{HNO_3}/\gamma_{AgNO_3}$			
		I	II	III	Mean
0.1900	0.0100	1.089	1.089	1.087	1.088
0.1750	0.0250	1.092	1.092	1.092	1.092
0.1500	0.0500	1.094	1.094	1.098	1.095
0.1250	0.0750	1.096	1.096	1.098	1.097
0.1000	0.1000	1.096	1.096	1.098	1.097
0.0750	0.1250	1.096	1.096	1.098	1.097
0.0500	0.1500	1.100	1.098	1.100	1.099
0.0250	0.1750	1.102	1.098	1.100	1.100
0.0100	0.1900	1.100	1.100	1.102	1.101

Table 19

Electromotive Force Measurements of the Cells

Ag, AgCl, HCl(0.2M), glass, $HNO_3(m_1)$, $AgNO_3(m_2)$, Ag

at Total Ionic Strength of 0.1 M

		Electrode I		Electrode II		Electrode III	
m_{HNO_3}	m_{AgNO_3}	E°	E	E°	E	E°	E
0.0950	0.0050	0.4718	0.3936	0.4716	0.3934	0.4716	0.3934
0.0875	0.0125	0.4718	0.4190	0.4716	0.4188	0.4716	0.4187
0.0750	0.0250	0.4718	0.4406	0.4716	0.4404	0.4716	0.4403
0.0625	0.0375	0.4718	0.4557	0.4716	0.4555	0.4716	0.4554
0.0500	0.0500	0.4718	0.4687	0.4716	0.4685	0.4716	0.4684
0.0375	0.0625	0.4718	0.4818	0.4716	0.4816	0.4716	0.4816
0.0250	0.0750	0.4718	0.4969	0.4716	0.4967	0.4716	0.4967
0.0125	0.0875	0.4718	0.5186	0.4716	0.5185	0.4716	0.5185
0.0050	0.0950	0.4718	0.5443	0.4716	0.5441	0.4716	0.5441

Table 20

Values of $\gamma_{HNO_3}/\gamma_{AgNO_3}$ Calculated from Table 19

m_{HNO_3}	m_{AgNO_3}	$\gamma_{HNO_3}/\gamma_{AgNO_3}$			
		I	II	III	Mean
0.0950	0.0050	1.052	1.052	1.052	1.052
0.0875	0.0125	1.056	1.056	1.058	1.057
0.0750	0.0250	1.060	1.060	1.062	1.061
0.0625	0.0375	1.060	1.060	1.062	1.061
0.0500	0.0500	1.062	1.062	1.064	1.063
0.0375	0.0625	1.062	1.062	1.062	1.062
0.0250	0.0750	1.062	1.062	1.062	1.062
0.0125	0.0875	1.064	1.062	1.062	1.063
0.0050	0.0950	1.062	1.062	1.062	1.062

error. In fact, for solutions of ionic strength equal to 0.1 molal, with the exception of the most acid solutions, the activity coefficient ratio is constant within the limits of experimental error.

Additional electromotive force measurements were made on the cell

Ag, AgCl, HCl(0.2M), glass, $HNO_3(m_1)$, $AgNO_3(m_1)$, Ag

where m_1 had values ranging from 0.005 to 1.0 M. These data, together with the calculated values of $\log \gamma_{HNO_3}/\gamma_{AgNO_3}$, are shown in Tables 21 and 22. From a plot of this ratio as a function of the square root of the ionic strength, such as is shown in Figure 8, it is evident that $\gamma_{HNO_3}/\gamma_{AgNO_3}$ becomes quite large for concentrated solutions. A similar plot may be made of the tabulated data for any concentration ratio of nitric acid to silver nitrate. Since the slope of curves of this type appears to become relatively constant as the ionic strength increases, the values of $\log \gamma_{HNO_3}/\gamma_{AgNO_3}$ in the more concentrated solutions as obtained by extrapolation are probably more nearly correct than those from the experimental measurements, in which the uncertainty in the "acid error" of the glass electrode increases with increasing ionic strength.

Table 21

Electromotive Force Measurements of the Cells

Ag, AgCl, HCl(0.2M), glass, $HNO_3(m_1)$, $AgNO_3(m_1)$, Ag

at Various Ionic Strengths

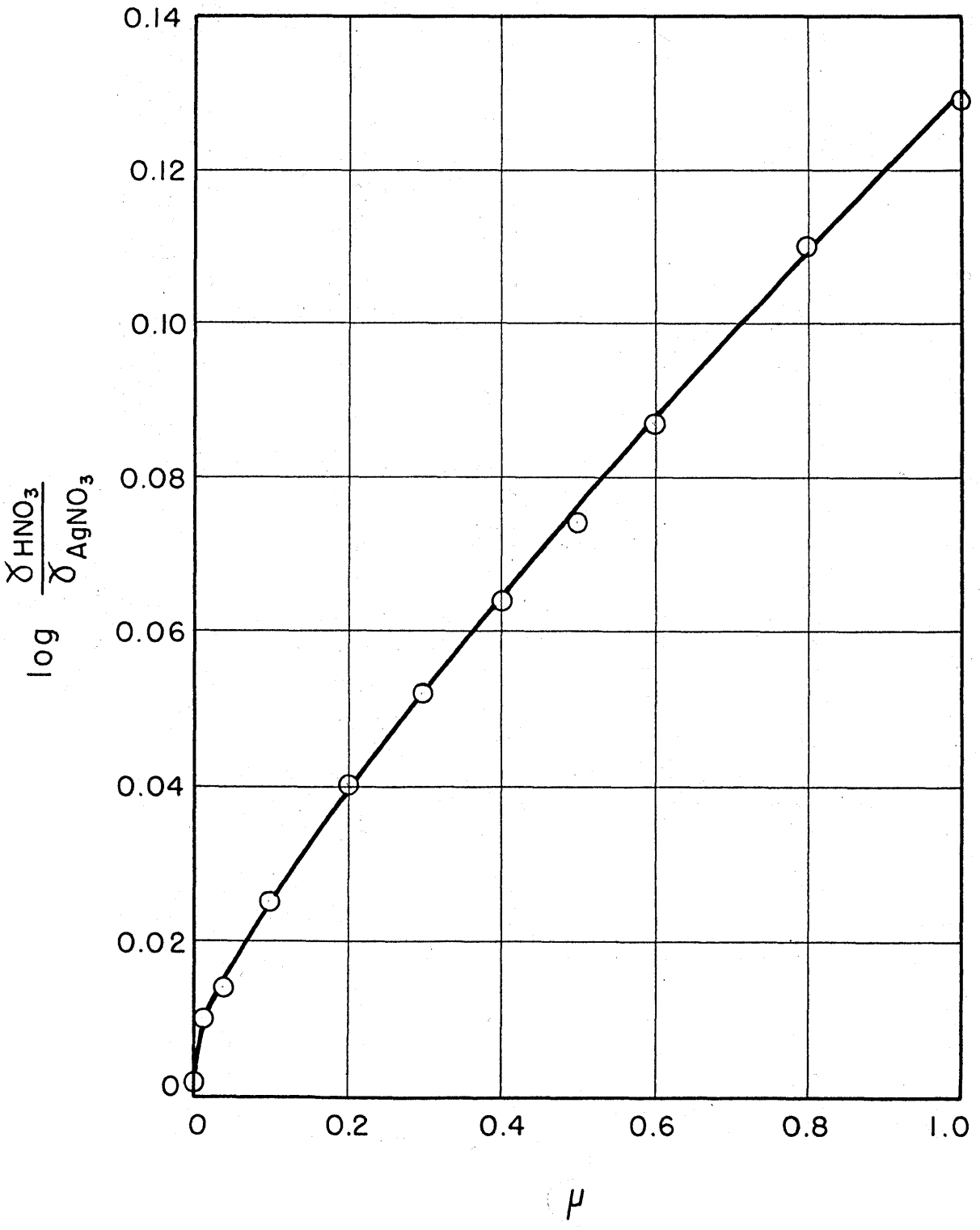
	Electrode I		Electrode II		Electrode III	
μ	E°	E	E°	E	E°	E
1.0	0.4722	0.4568	0.4720	0.4567	0.4719	0.4566
0.8	0.4721	0.4591	0.4719	0.4590	0.4718	0.4588
0.6	0.4720	0.4616	0.4718	0.4615	0.4717	0.4614
0.4	0.4719	0.4642	0.4717	0.4642	0.4716	0.4641
0.3	0.4719	0.4657	0.4717	0.4656	0.4716	0.4655
0.1	0.4718	0.4688	0.4716	0.4686	0.4715	0.4686
0.04	0.4718	0.4702	0.4716	0.4700	0.4715	0.4699
0.01	0.4718	0.4712	0.4716	0.4710	0.4715	0.4709
0.005	0.4718	0.4716	0.4716	0.4713	0.4715	0.4712

Table 22

Values of log $\gamma_{HNO_3}/\gamma_{AgNO_3}$ Calculated from Table 21

	log $\gamma_{HNO_3}/\gamma_{AgNO_3}$			
μ	I	II	III	Mean
1.0	0.130	0.129	0.129	0.129
0.8	0.110	0.109	0.110	0.110
0.6	0.088	0.087	0.087	0.087
0.4	0.065	0.063	0.063	0.064
0.3	0.052	0.052	0.052	0.052
0.1	0.025	0.025	0.025	0.025
0.04	0.014	0.014	0.014	0.014
0.01	0.005	0.005	0.005	0.005
0.005	0.002	0.003	0.002	0.002

Fig. 8



Application to Ion Exchange Data

By combination of the ion exchange data for the silver-hydrogen exchange[1] with the activity coefficient ratios of nitric acid and silver nitrate in binary aqueous solutions, the equilibrium constant

$$K = \frac{a_{HNO_3}\ a_{Ag\ Res}}{a_{AgNO_3}\ a_{H\ Res}}$$

and the activity coefficients of each of the components of the resin phase may be calculated for this exchange in the same manner as for the sodium-hydrogen exchange[2].

In each of these exchange reactions, the initial ionic strength of the aqueous solution was adjusted in such a manner as to give an equilibrium solution of ionic strength as nearly as possible equal to unity. However, due to the relatively large amount of electrolyte which was adsorbed by the resin, the resulting ionic strengths of the equilibrium solutions in some cases differed from unity by as much as five percent. Since the ratio of the activity coefficients of nitric acid and silver nitrate, for any given concentration ratio, varies greatly with the ionic strength of the solution, it was not possible to use the values of $\gamma_{HNO_3}/\gamma_{AgNO_3}$ for solutions of ionic strength equal to unity; rather, in each case this ratio

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1. This Thesis, Part I, page 21.

2. This Thesis, Part II, page 33.

was corrected to correspond to the actual ionic strength of that particular equilibrium solution.

The data used in the calculation of the values of K'_c for this series of exchange reactions are presented in Table 23, and the calculated values of log K'_c are plotted as a function of resin composition in Figure 9. In contrast with the corresponding curve representing the results of the sodium-hydrogen exchange, the slope of this curve has a positive value throughout its length. This fact leads to values of the activity coefficients of the components of the resin phase which are greater than unity. These activity coefficients, obtained at various compositions by means of graphical integration, are shown in Table 24. The value of the equilibrium constant was found to be 13.7.

By combination of these results with those of the sodium-hydrogen exchange, we may calculate that the equilibrium constant for the exchange

$$AgNO_3 + Na\ Resin = Na\ NO_3 + Ag\ Resin$$

should be 13.7/1.73 or 7.90.

Table 23

Silver-Hydrogen Exchange

Initial Resin	$N_{Ag\ Res}$ at Equilibrium	Concentrations at Equilibrium HNO_3	Concentrations at Equilibrium $AgNO_3$	K_c	$\frac{\gamma^2_{HNO_3}}{\gamma^2_{AgNO_3}}$	K_c'
H Res	0.932	0.4462	0.5094	12.02	1.808	21.73
H Res	0.713	0.7462	0.2182	8.47	1.765	14.95
H Res	0.701	0.7344	0.2073	8.30	1.759	14.59
H Res	0.538	0.8360	0.1310	7.45	1.745	13.00
H Res	0.477	0.8551	0.1042	7.12	1.736	12.35
H Res	0.177	0.9341	0.0327	6.17	1.697	10.48
Ag Res	0.981	0.2558	0.7111	18.29	1.839	33.65
Ag Res	0.979	0.2523	0.7073	17.02	1.838	31.28
Ag Res	0.935	0.4449	0.4993	12.65	1.805	22.84
Ag Res	0.815	0.6594	0.3031	9.63	1.780	17.14
Ag Res	0.685	0.7680	0.2007	8.32	1.762	14.65
Ag Res	0.568	0.8321	0.1422	7.69	1.751	13.46
Ag Res	0.534	0.8442	0.1264	7.67	1.745	13.38

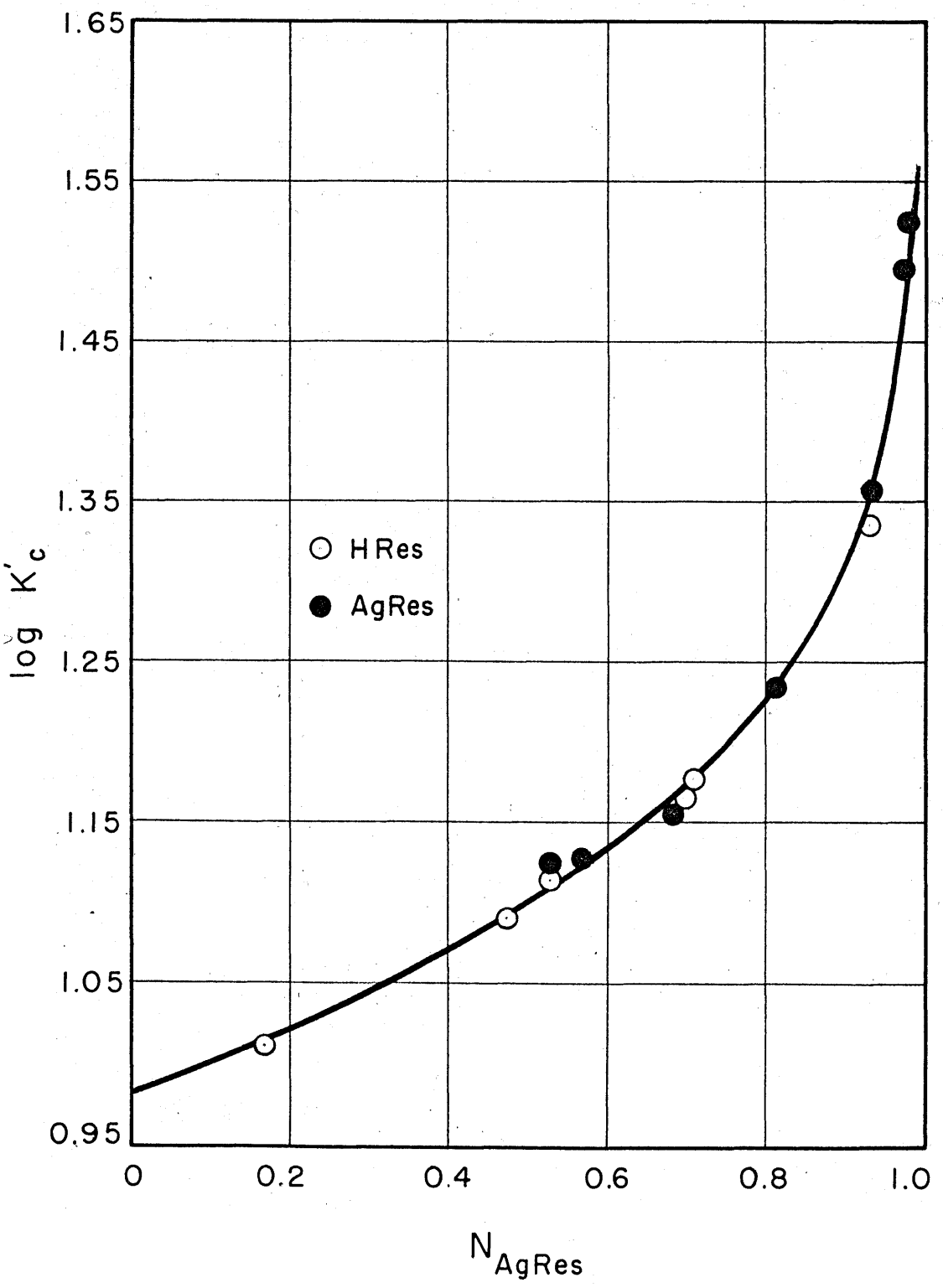
Table 24

Activity Coefficients of Silver Resin and of Hydrogen Resin at Various Resin Compositions

$N_{Ag\ Res}$	$f_{Ag\ Res}$	$f_{H\ Res}$
0.0	1.417*	1.000
0.1	1.350	1.003
0.2	1.293	1.012
0.3	1.240	1.023
0.4	1.193	1.045
0.5	1.155	1.074
0.6	1.117	1.116
0.7	1.087	1.177
0.8	1.054	1.291
0.9	1.024	1.531
1.0	1.000	3.05*

*Extrapolated values

Fig. 9


1.65
1.55
1.45
1.35
1.25
1.15
1.05
0.95
log K'c
HRes
AgRes
0
0.2
0.4
0.6
0.8
1.0
N AgRes

Summary

The behavior of a low-resistance type glass electrode in acid solutions has been calibrated by means of electromotive force measurements of cells of the type

Ag, AgCl, HCl(0.2M), glass, HCl(m), AgCl, Ag.

This electrode was then incorporated in the cells

Ag, AgCl, HCl(0.2M), glass, $HNO_3(m_1)$, $AgNO_3(m_2)$, Ag,

which were used to determine the ratios of the activity coefficients of nitric acid and silver nitrate in solutions of ionic strength ranging from 0.005 to 1.0 molal.

These activity coefficient data were combined with ion exchange data for the silver-hydrogen exchange, and values of the activity coefficients of the components of the resin phase and the equilibrium constant for the reaction

$$AgNO_3 + H\ Resin = HNO_3 + Ag\ Resin$$

were calculated. In contrast with the sodium-hydrogen exchange, the activity coefficients of the resin components were found to be greater than unity.

POSSIBILITIES FOR FUTURE WORK

The good agreement between the calculated values of the equilibrium constant and the activity coefficients of the resin phase components for the two series of sodium-hydrogen exchange reactions, in which the ionic strengths of the aqueous solutions were maintained constant at 1.0 molal and 0.3 molal, respectively, suggests that further exchange experiments might well be carried out at other ionic strengths. Although, since the activity coefficient data for sodium chloride are less reliable than the ion exchange data, perfect agreement is hardly to be expected, it would nevertheless be of interest to determine whether or not the calculated equilibrium quotient and resin phase activity coefficients would remain approximately constant.

Perhaps more conclusive verification of this method of treatment of ion exchange data could be obtained by the performance of additional silver-hydrogen exchange experiments, since the activity coefficient ratios of these electrolytes have been determined by direct experiment. Also, the quantities of electrolytes adsorbed by resins of high silver content has been found to be relatively very great, and it should be determined whether or not the exchange reaction is affected by this adsorption.

By means of the same type of electromotive force measurements which were used to determine the activity co-

efficient data for solutions of nitric acid and silver nitrate, it should be possible to determine the activity coefficient ratios of mercurous nitrate to nitric acid, palladous chloride to hydrochloric acid and others. These data also could then be combined with ion exchange data for the same electrolytes, as a further test of the method of treatment of ion exchange data described in Part II of this thesis.

If it can be verified that the values of K and of the activity coefficients of the resin phase components at a given composition are actually constant, and therefore independent of side reactions such as absorption of water or adsorption of electrolyte by the resin, several interesting possibilities are apparent. If the activity coefficient ratios of the components of the aqueous solution are known at any one ionic strength, they may be calculated by this method, for any concentration ratio at any other ionic strength, as they constitute the only unknown in the equation

$$K = K_c' \frac{\gamma^2_{A^+An^-}}{\gamma^2_{B^+An^-}}$$

Since several investigators have successfully conducted ion exchange experiments in which the ionic strength of the aqueous solution was as small at 10^{-3} molal, at which concentration the ratio of the activity coefficients of the electrolytes is in most cases only very slightly different

from unity, this method of calculation of activity coefficient ratios is almost universally applicable. If several series of exchanges in very dilute solutions were performed, the true values of K and of $f_{A\ Res}/f_{B\ Res}$ at any concentration ratio could be determined by extrapolation methods.

The same method should be capable of extension also to non-aqueous solutions. It is true that, since different standard states are chosen for such solutions, the values of K for the exchange would probably be different, but the values of the resin phase activity coefficients should be independent of the nature of the solvent. Then, in a treatment analogous to that used for aqueous solutions, the equilibrium expression would take the form,

$$K = K_c \cdot \frac{f_{B\ Res}}{f_{A\ Res}} \cdot \frac{\gamma^2_{A^+An^-}}{\gamma^2_{B^+An^-}} = K''_c \cdot \frac{\gamma^2_{A^+An^-}}{\gamma^2_{B^+An^-}}$$

Since the values of the resin phase activity coefficients would be known from data in aqueous solutions, and the value of K_c could be determined by experiment, the value of K might be found by extrapolation to infinite dilution of a plot of K''_c as a function of the ionic strength, for solutions of any fixed concentration ratio. The ratio of the solution phase activity coefficients, as the only remaining unknown quantity, might be calculated.

APPENDIX

The entire reaction that occurs in the cell

Ag, AgCl, HCl(m_1), glass, HCl(m_2), AgCl, Ag

is not definitely known. Dole (11, 12) postulates that hydrated protons pass through the glass membrane, which means, in effect, that hydrochloric acid and water are transferred from one solution to the other. This hypothesis would lead to the following equation for the total potential of the electrode, in which x is the number of molecules of water transported per proton:

$$E = -\frac{RT}{F} \ln \frac{a_{HCl(2)}}{a_{HCl(1)}} - \frac{xRT}{F} \ln \frac{a_{H_2O(2)}}{a_{H_2O(1)}}$$

Since the acid used in the electrode is very dilute, this equation is equivalent to Dole's expression for the deviation of the glass electrode from the ideal behavior of the hydrogen electrode:

$$\Delta E = \frac{xRT}{F} \ln a_{H_2O}$$

This theory makes it possible to explain, at least qualitatively, the data which are obtained when the glass electrode is used in non-aqueous or in concentrated aqueous solutions. However, it neglects the "asymmetry potential", which is known not to be constant for an electrode over a period of time but to vary by as much as several millivolts, and it does not account for the difference in value of the "acid error" when

an electrode is immersed successively in two solutions of the same water activity but of different hydrogen ion activity. For example, the "acid error" is not the same in concentrated solutions of hydrochloric and sulfuric acids having the same water activity (14,20).

Laug, in his investigations (21), found that thorough drying of the outside of a glass electrode increases the "asymmetry potential" of the electrode, as measured by the cell

$$Hg/Hg_2Cl_2, \text{ sat.KCl//Soln.A/glass/PO}_4 \text{ buffer, pH} = 6.5// \text{sat.KCl, } Hg_2Cl_2/Hg$$

in which Solution A represents one of a series of acid test solutions. The increase in this potential was found to be proportional to the time of drying, and a three-to four-hour period of soaking in water was found necessary to recondition the membrane. He concludes that the state of hydration of the outside layer of the membrane affects the ability of the glass electrode to function as a hydrogen electrode. Yoshimura (22) observed a similar effect when either side of the membrane was dried. That is, the "asymmetry potential" was negative when the outer surface was dried, and positive when the inner surface was dried. He also found that the ability of a glass electrode to function as a hydrogen electrode improves with the time of soaking in water.

In order that the anomalous behavior of the glass electrode might be further studied, electromotive measurements were made of the cell

Ag, AgCl, HCl(0.2M), glass, HNO_3(0.05M), $AgNO_3$(0.05M), Ag after the glass electrode had been soaked in various solutions for a period of at least 24 hours. The water activities of these solutions were calculated from vapor pressure data given in the International Critical Tables. A quantity ΔE may be defined as the difference between the potential of the above cell as measured after soaking the glass electrode in a given solution, and the potential after soaking it in water. This quantity is actually the "asymmetry potential" as defined by Laug (21). From the results of these experiments, which are presented in Table 25, it is seen that for the salt solutions, ΔE increases with decreasing water activity of the solutions in which the electrode has been soaked, a fact which is in accord with the conclusions of Laug and of Yoshimura. However, in the acid solutions (with the exception of sulfuric acid), ΔE is seen to be quite large and variable even for solutions in which the water activity is close to unity. A possible explanation is that acid solutions, due to the high mobility of the hydronium ion, are able to effect a more rapid partial dehydration of the glass membrane. Sinclair and Martell (14) also have observed that a constant potential is not obtained when the glass electrode is used in concentrated hydrochloric acid solutions.

In a series of similar experiments, electromotive force measurements were made of the cells

Table 25

Asymmetry Potential of the Glass Electrode

Solution	a_{H_2O}	Period of soaking (days)	E(volts)
1 M $NaNO_3$	-	1	0.0008
Sat. NH_4Cl	0.79	2	0.0037
Sat. $NaNO_3$	0.73	1	0.0041
Sat. $Ca(NO_3)_2$	0.51	3	0.0073
Sat. $CaCl_2$	0.31	1	0.0123
1 M HCl	0.962	1	0.0021
	0.962	2	0.0024
	0.962	3	0.0047
	0.962	4	0.0064
0.5 M H_2SO_4	0.982	2	0.0000
1 M $HC_2H_3O_2$	-	1	0.0005
	-	2	0.0009
1 M HNO_3	-	1	0.0007
	-	2	0.0023

Ag, AgCl, HCl(0.2M), glass, HCl(m_1), AgCl, Ag

where m_1 = 0.1 or 1.0. The E^o value for the glass electrode in each case may be calculated, since activity coefficient data are available for hydrochloric acid solutions. The E^o values calculated from the measurements which were made after the electrode had been soaked in water were -0.1127 v. in 0.1 M HCl and -0.1102 v. in 1 M HCl. After soaking for a period of 48 hours in a saturated solution of calcium nitrate, the values were -0.1073 v. in 0.1 M HCl and -0.1046 v. in 1 M HCl. The "asymmetry potential" change is seen to be approximately constant (5.5 $\pm$ 0.1 mv.), i.e., independent of the solution which is used for its measurement. The "acid error" is also seen to be approximately constant (2.6 $\pm$ 0.1 mv.), i.e., independent of the degree of hydration of the glass.

These experiments, as well as the data from the literature, seem to indicate that the potential which is produced by the glass electrode is due to several causes. The major contribution is, of course, that which results from the hydrogen ion activity of the solution. There are additional potentials, however, which are functions of the degree of hydration of the surfaces of the glass membrane and of the acidity of the solution.

A mechanism, original with the present author, may be postulated for the above cell, which seems preferable to that suggested by Dole, and which takes these factors into consid-

eration. It is recognized that glass is not crystalline in nature, but that it is in reality a supercooled liquid. Soft glass, such as is used for electrodes, may be thought of as a very viscous solution of silicates, which conducts the electric current in the usual manner, but which has a high resistance because of the extremely low mobility of the ions. That the surface regions of the glass membrane are able to occlude, or adsorb, appreciable quantities of water is shown by the experiments described above. It is thus reasonable to suppose that they may also adsorb small quantities of electrolyte. The following equations, in which "1" and "2" represent the solutions and "a" represents adsorbed material, may be used to represent the cell reaction.

$$Cl^-_{(1)} + Ag = AgCl + e$$

$$H^+_{(1a)} + \tfrac{1}{2}\, SiO_3^= + \tfrac{1}{2}\, H_2O_{(1a)} = \tfrac{1}{2}\, Si(OH)_4$$

$$AgCl + e = Ag + Cl^-_{(2)}$$

$$\tfrac{1}{2}\, Si(OH)_4 = \tfrac{1}{2}\, SiO_3^= + \tfrac{1}{2}\, H_2O_{(2a)} + H^+_{(2a)}$$

The overall reaction is then

$$H^+_{(1a)} + Cl^-_{(1)} + \tfrac{1}{2}\, H_2O_{(1a)} = H^+_{(2a)} + Cl^-_{(2)} + \tfrac{1}{2}\, H_2O_{(2a)}$$

The Nernst equation takes the form

$$E = -\frac{RT}{F} \ln \frac{a_{H^+(2a)}\; a_{Cl^-(2)}\; a^{\frac{1}{2}}_{H_2O(2a)}}{a_{H^+(1a)}\; a_{Cl^-(1)}\; a^{\frac{1}{2}}_{H_2O(1a)}}$$

An equivalent expression is

$$E = -\frac{RT}{F}\ln\frac{a_{HCl(2)}}{a_{HCl(1)}} - \frac{RT}{F}\ln\frac{a_{H^+(2a)}}{a_{H^+(2)}}\Big/\frac{a_{H^+(1a)}}{a_{H^+(1)}} - \frac{RT}{2F}\ln\frac{a_{H_2O(2a)}}{a_{H_2O(1a)}}$$

The first logarithmic term in the expression represents the behavior of a perfect hydrogen electrode. The third term represents the potential which is dependent upon the state of hydration of the surfaces of the glass membrane. The second term represents the relationship, for each surface, between the activity of the hydrogen ion in the bulk of the solution and its activity in the surface of the electrode. The presence of such a term is in qualitative agreement with adsorption data for electrolytes, as it is known that relatively greater adsorption occurs in dilute solutions.

Unfortunately, since the activities of adsorbed water and of hydrogen ion are unknown, this equation cannot at present be checked quantitatively, but the relative magnitude of each of the terms may be estimated. For electrodes which contain dilute acid and are stored in water between periods of use, the third term of this expression will be approximately zero. If the electrode is used in non-aqueous or in concentrated aqueous solutions, this term will become larger as the time of immersion in the solution increases, as was the case in the experiments of Sinclair and Martell (14). The value of the second term of the expression will be dependent upon the relative adsorbability of the hydrogen ion in the inner

and outer solutions. When the electrode is placed in dilute aqueous solutions, its value will be zero. In concentrated aqueous solutions, and apparently in non-aqueous solutions, the relative adsorption of hydrogen ion is smaller than in the dilute inner solution and the value of this term becomes larger, being equal in every case to the measured "acid error".

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